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OF THE
ROYAL SOCIETY
OF NEW SOUTH WALES
FOR
1945
(INCORPORATED 1881)

VOLUME LXXIX
Parts I-IV

EDITED BY
D. P. MELLOR, D.Sc.
Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

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GLOUCESTER AND ESSEX STREETS

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* Published April 12, 1946.
† Published June 19, 1946.
‡ Published August 12, 1946.

* Published October 28, 1946.

NOTICE.

The Royal Society of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862–5, pp. 374, out of print.								
Vols.	I–XI	Transactions of the Royal Society, N.S.W., 1867–1877						,,
Vol.	XII	Journal and Proceedings	,,	,,	1878,	pp.	324,	price 10s. 6d.
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Royal Society of New South Wales

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LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

as at March 1, 1946

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney.
1938	P 2	‡Albert, Adrien, Ph.D. *Lond.*, B.Sc. *Syd.*, A.R.I.C. *Gt. B.*, Commonwealth Research Fellow in Organic Chemistry, University of Sydney ; p.r. " Greenknowe," Greenknowe-avenue, Potts Point.
1935		‡Albert, Michel Francois, " Boomerang," Billyard-avenue, Elizabeth Bay.
1898		‡Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		‡Alldis, Victor le Roy, L.S., Registered Surveyor, Box 57, Orange, N.S.W.
1909	P 12	‡Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, " Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1945		Armytage, Jean, M.B., B.S., M.R.A.C.P., 32A Rawson-street, Epping.
1930		Aston, Ronald Leslie, B.E. *Syd.*, M.Sc., Ph.D. *Cantab.*, A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney ; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 1	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill ; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1940	P 4	Beattie, Joan Marian (Mrs.), B.Sc., 219 Victoria-road, Gladesville.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, " Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., Rosebery-road, Killara.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (*Oxon.*), 37 Museum-road, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney ; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale ; p.r. 26A Wolseley-road, Mosman.
1938	P 1	Black, Una Annie Frazer (Mrs.), B.Sc., 401 St. Kilda-road, Elwood, S.3, Victoria.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., " Holmleigh," Cecil-avenue, Pennant Hills.
1933	P 25	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., International Wool Secretariat, Grand Building, Trafalgar Square, London, W.C.2. (President, 1935.)
1939	P 8	Bosworth, Richard Charles Leslie, D.Sc. *Adel.*, Ph.D. *Camb.*, F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont ; p.r. 41 Spencer-road, Killara.
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney ; p.r. 19 Handley-avenue, Thornleigh.

Elected.		
1940		Brigden, Alan Charles, B.Sc., 8 Clifford-avenue, Manly.
1919	P 1	Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney ; p.r. 13 Findlay-avenue, Roseville.
1942		Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
1935	P 4	Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
1913	P 22	Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
1940		Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1940	P 1	Cane, Reginald Frank, M.Sc., A.A.C.I., General Motors-Holdens Ltd., Fishermen's Bend, Melbourne, Victoria ; p.r. 2 David-street, St. Kilda, S.2.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 2	‡Carey, Samuel Warren, D.Sc., Government Geologist, Department of Mines, Hobart, Tasmania.
1903	P 5	‡Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge ; Burradoo, N.S.W.
1945		Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster Laboratory ; p.r. Flat 4, 13 Milson-road, Cremorne.
1944		Cavill, George William Kenneth, B.Sc., Department of Chemistry, Technical College, Harris-street, Ultimo ; p.r. 40 Chandos-street, Ashfield.
1913	P 4	Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S. ; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
1940		Chambers, Maxwell Clark, B.Sc., c/o J. and E. Atkinson Pty. Ltd., 469-75 Kent-street, Sydney.
1913	P 21	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1940		Clarke, Ronald Stuart, B.A., 28 Beecroft-road, Beecroft.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.Sc., A.I.F., 80 "St. James," Stanley-street, Sydney.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 34 Euroka-street, Northbridge.
1940	P 2	Colditz, Margaret Joyce, B.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 14 Barwon-road, Lane Cove.
1940	P 1	Cole, Joyce Marie, B.Sc., 14 Barwon-road, Lane Cove.
1940		Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1945		Coombes, Arthur Roylance, A.S.T.C. (Chem.), 14 Georges River-road, Croydon.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College ; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1937	P 8	Cornforth, Rita Harriet, D.Phil. (*Oxon.*), M.Sc. (*Syd.*), c o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
1940		Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
1909	P 7	‡Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1941	P 1	Craig, David Parker, Lecturer in Inorganic Chemistry, University of Sydney ; p.r. 62 Springdale-road, Killara.
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay ; p.r. 101 Villiers-street., Rockdale.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		‡Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.

Elected.		
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 8	Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 28	Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, Technical College, Sydney.
1945		Eade, Ronald Arthur, B.Sc., 13 Steward-street, Leichhardt.
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.R.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940. Hon. Secretary.)
1940		Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
1937		English, James Roland, L.S., Water Conservation and Irrigation Commission, Sydney.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1944		Erhart, John Charles, Chemical Engineer, 33 Beaconsfield-parade, Lindfield.
1908		‡Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. *Lond.*, A.R.A.I.A., 6 Major-street, Coogee.
1944		Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 8 Courland-street, Randwick.
1921		Farnsworth, Henry Gordon, "Rothsay," 90 Alt-street, Ashfield.
1939		Faull, Norman Augustus, B.Sc., A.Inst.P., c.o. National Standards Laboratory, University Grounds, City-road, Chippendale.
1909	P 7	‡Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Professor of Chemistry in the University of Sydney. (President, 1919.)
1940		Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1933		Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		‡Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 6 "Trinity Court," Telopea-street, Wollstonecraft.
1940		Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1944		Friend, James Alan, 16 Kelburn-road, Roseville.
1945		Furst, Hellmut Friedrich, B.D.S. (*Syd.*), D.M.D. (*Hamburg*), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.
1935	P 2	Garretty, Michael Duhan, M.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1942	P 3	Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1940		Gillis, Richard Galvin, 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1935		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.
1936		Goulston, Edna Maude, B.Sc., Third Officer, W.R.A.N.S., Navy Office, Melbourne.
1940		Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.

Elected.		
1945		Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 15A Wharf-road, Longueville.
1892		‡Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
1940	P 2	Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney; p.r. 12 Countess-street, Mosman.
1905	P 6	‡Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1929		Hawley, J. William, J.P., Financial Agent.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 101 Essex-street, Epping.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945		Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd.; p.r. 10 Cremorne-road, Cremorne.
1938	P 4	Hill, Dorothy, M.Sc. *Q'ld.*, Ph.D. *Cantab.*, Geological Research Fellow, University of Queensland, Brisbane.
1918		Hindmarsh, Percival, M.A. B.Sc.Agr., Principal, Hurlstone Agricultural High School, Glenfield.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), "St. Cloud," Beaconsfield-road, Chatswood.
1916		Hoggan, Henry James, A.M.I.M.E. *Lond.*, A.M.I.E. *Aust.*, Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 4	Hughes, Gordon Kingsley, B.Sc., Lecturer in Chemistry, University of Sydney.
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1943		Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney; p.r. 96 Roseville-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1940		Johns, Thomas Harley, 130 Smith-street, Summer Hill.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1911		Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.
1935		Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 90 Loch Maree-street, Maroubra.
1943		Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.

Elected.		
1945		Laing, Norma Dorothy, B.Sc., Biochemist, 58, Hopetoun-avenue, Vaucluse.
1939		Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., P.O. Box 21, Concord.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 55	‡Lions, Francis, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, University of Sydney.
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 3	Lipson, Menzie, B.Sc., A.A.C.I., Chemist, c/o Department of Textile Industry, Leeds University, Leeds 2, England.
1940	P 1	Lockwood, William Hutton, B.Sc., c.o. Department of Post-War Reconstruction, Hotel Acton, Canberra, A.C.T.
1906		‡Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1943		Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 8 Boronia-avenue, Wollstonecraft.
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943		McCoy, William Kevin, Analytical Chemist, R.A.A.F.; p.r. 16 Bishop's-avenue, Randwick.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	‡McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	‡McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 2	McKenzie, Hugh Albert, B.Sc., Assistant Research Officer, C.S.I.R.; p.r. 52 Bolton-street, Guildford.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Technological Museum, Harris-street, Ultimo; p.r. 14 Orwell-street, Potts Point.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1943		McNamara, Barbara Joyce (Mrs.), M.B., B.S., 110 Elizabeth Bay-road, Elizabeth Bay.
1940		Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1935	P 1	Maze, Wilson Harold, M.Sc., Lecturer in Geography, University of Sydney.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 23	Mellor, David Paver, D.Sc., F.A.C.I., Lecturer, Chemistry Department, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42 Joint Hon. Secretary.)
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1940		Mercer, Edgar Howard, McMaster Laboratory, Parramatta-road, Glebe.
1928		Michell, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1943		Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street, Rockdale.
1945		Morris, Samuel, A.S.T.C. (Chem.), A.A.C.I., F.C.S.G.B., 217 Burns Bay-road, Lane Cove.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 27	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
1944		Moye, Daniel George, Chemist, "Whiporie," Holland-street, Cronulla.
1915		Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., F.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Government House, Port Moresby, Papua.

Elected.		
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
1943		Neuhaus, John William George, c/o Meggitt Ltd., Parramatta.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. 59 Victoria-road, Parramatta.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1945		Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Secretary, Linnean Society of N.S.W., Science House, Gloucester-street, Sydney.
1920	P 4	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 16	Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
1935	P 1	O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1921	P 6	Osborne, George Davenport, D.Sc. *Syd.*, Ph.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney. (President, 1944.)
1920	P 74	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 67 Park-avenue, Roseville. (President, 1935.)
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliff.
1943		Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		‡Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1945		Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1945		Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
1893		‡Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 6	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940	P 1	Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Mineral Resources Survey, Department of Supply and Shipping, Census Building, Canberra, A.C.T.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1939	P 14	Ritchie, Ernest, B.Sc., Chemistry Department, University of Sydney.
1939	P 3	Robbins, Elizabeth Marie (Mrs.), M.Sc., 36 Cambridge-street, Epping.
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.

Elected.		
1940		Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1945		Rountree, Phyllis Margaret, M.Sc. *Melb.*, Dip.Bact. *Lond.*, 25 Elizabeth Bay-road, Elizabeth Bay.
1945		Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory; p.r. 83 Woniora-road, Hurstville.
1945		Sampson, Aileen (Mrs.), Sc.Dip. (A.S.T.C., 1944), 54 Young-street, Croydon.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 2	Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1940		Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, 2 Edward-street, Gordon.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
1945		Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1945	P 1	Simmons, Lewis Michael, B.Sc. (Hons.) *Lond.*, A.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill.
1900		‡Simpson, R. C., Park-avenue, Roseville.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, New College, Oxford, England.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	‡Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney.
1940		Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1901	P 16	‡Sussmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. *Adel.*, c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.

Elected		
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Flight-Lieutenant, R.A.A.F., M.Sc., A.Inst.P., 1 Valley-road, Lindfield.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.
1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	‡Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney. (President, 1930.)
1943		Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1945		Walters, Laurence Gordon, B.Sc., Flat 3, 33 Gould-street, Bondi.
1913	P 5	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 15 Belmore-road, Penshurst.
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c.o. Australian Museum, College-street, Sydney.
1919	P 1	Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 6	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Reader in Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1944		Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
1945		Webster, Evelyn May, B.Sc., Chemist, 2 Buena Vista-avenue, Mosman.
1920		Wellish, Edward Montague, M.A., Emeritus Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1940	P 1	White, Douglas Elwood, M.Sc., D.Phil., University of Western Australia, Nedlands, W.A.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.
1944	P 1	Willis, John Bryan, B.Sc., Demonstrator in Chemistry, University of Sydney; p.r. Flat 2, Russell Hall, 17 Mount-street, Coogee.
1945		Willis, Jack Lehane, B.Sc., Flat 5, "Narooma", Hampden-street, North Sydney.
1943		Winch, Leonard, B.Sc., Chief Chemist, Fielder's General Products Ltd., P.O. Box 143, Tamworth, N.S.W.
1940		Wogan, Samuel James, Range-road, Sarina, North Queensland.

Elected.		
1936	P 3	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory.
1906	P 12	‡Woolnough, Walter George, D.Sc., F.G.S., 9 Lockerbie Court, East St. Kilda, Victoria. (President, 1926.)
1945		Wright, Barbara, B.Sc., Biochemist, "Derribong," Ada-avenue, Wahroonga.
1916		Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 16 Barrack-street, Sydney; p.r. "Wanawong," Castle Hill, N.S.W.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.

Honorary Members.

Limited to Twenty.

1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1915	Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.

Obituary, 1945-1946.

1924	Frederick Stapleton Mance.
1903	Richard Old.
1918	John Powell.
1928	Allan Clunies Ross. (Hon. Treasurer.)
1922	Thomas Hodge-Smith.
1924	Leslie Vickery Waterhouse.
1922	James T. Wilson.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.

"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.

"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.

"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (This Journ., 1936, *70*, 39.)

1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (This Journ., 1937, *71*, 68.)

1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (This Journ., 1938, *71*, 503.)

1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (This Journ., 1939, *73*, 41.)

1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (This Journ., 1940, *74*, 283.)

1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (This Journ., 1941, *75*, 47.)

1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.

1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.

1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.

1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 *to* 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.

1879 *George Bentham, C.M.G., F.R.S.

1880 *Professor Thos. Huxley, F.R.S.

1881 *Professor F. M'Coy, F.R.S., F.G.S.

1882 *Professor James Dwight Dana, LL.D.

1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.

1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.

1886 *Professor L. G. De Koninck, M.D.

Awarded.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., SC.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., SC.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.SC., F.G.S.
1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
1909 *Dr. Walter E. Roth, B.A.
1912 *W. H. Twelvetrees, F.G.S.
1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.SC., F.R.S.
1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., SC.D., D.SC., F.R.S., F.G.S.
1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.SC.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.SC., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, D.SC., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.SC., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, M.A., D.SC., SC.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
1933 Walter George Woolnough, D.SC., F.G.S., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, D.SC., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.SC., B.E., University of Adelaide.
1937 J. T. Jutson, B.SC., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 Professor H. C. Richards, D.SC., The University of Queensland, Brisbane.
1939 C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, M.B., B.S., D.SC., F.R.S., Anatomy Department, University of Manchester, England.
1942 William Rowan Browne, D.SC., Reader in Geology, The University of Sydney, N.S.W.
1943 Walter Lawry Waterhouse, M.C., D.SC.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.SC., F.R.S., University of Melbourne, Carlton, Victoria.
1945 Professor William Noel Benson, B.A., D.SC., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.
1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.
1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."

Awarded.

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.

1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.

1940 G. J. Burrows, B.Sc., University of Sydney.

1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.

1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.

ISSUED APRIL 12, 1946

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OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

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Part I

PRESIDENTIAL ADDRESS

By G. D. OSBORNE, D.Sc., Ph.D.

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Delivered to the Royal Society of New South Wales, April 4, 1945.

CONTENTS.

PART I. THE SOCIETY'S ACTIVITIES DURING THE PAST YEAR.

Although the actual cessation of hostilities between Germany and the Allies has not been officially proclaimed, we can this evening have some sense of relief that the European phase of the war is nearly concluded, and we earnestly hope that the annual meeting of 1946 will be held in the knowledge that the final overthrow by the Allied Nations of the remaining enemy will not long be delayed.

We may justly feel a certain degree of satisfaction in that during long ordeal of war the Royal Society of New South Wales has endeavoured to maintain, by its support of research work and general scientific activity, a sanity of outlook upon life when world affairs have been so unstable.

In spite of the conditions prevailing, we have had a very successful year and meetings have been well attended. This has been due partly to the fact that a fairly wide scope of interest has been provided for in the agenda from month

to month, and partly due to the relatively large number of lecturettes that have been given at the ordinary meetings. The speakers in this connection have been Sir Walter McNicol, Professor Elkin, Professor F. S. Cotton, Drs. Reimann, Lions and Aston and Messrs. Giovanelli, Maze and Thorne.

During the year five popular lectures drew large attendances, and this activity might well be extended, as there is amongst a certain section of the community a growing interest in science. The lectures were:

15th June.—" Man and Heredity ", by A. N. Colefax, B.Sc.

20th July.—" Fuels in the Service of Man ", by J. A. Dulhunty, B.Sc.

17th August.—" Man and Metals ", by F. P. Dwyer, M.Sc.

21st September.—" Man and the Expanding Universe ", by Rev. Father O'Connell, S.J.

29th October.—" My Lady's Perfume ", by F. R. Morrison, F.C.S., A.A.C.I.

On August 2nd a very successful symposium, arranged by Dr. Mellor, on the subject " Trace Elements in Plant and Animal Nutrition ", was held before a crowded audience. After some introductory remarks upon the geological aspects by the President, the main speakers were Professor Ashby, Dr. Hallsworth and Dr. Still.

In view of the impropriety of holding purely social functions during the war period, it was felt that some fostering of fellowship among members would be achieved by arranging a semi-social fixture. This took the form of an Exhibition of scientific photographs and some miscellaneous specimens, which was held, by courtesy of David Jones Ltd., at their Art Gallery, and proved successful, being attended by a considerable and representative number of members, accompanied by relatives and friends. For the loan of photographs and exhibits the Council is grateful to several institutions and persons. It may be possible to develop the idea of the Society arranging or sponsoring a periodical, perhaps biennial, exhibition of scientific photographs. Such could be open to the public and brought before the notice of students generally and scholars of secondary schools. In this way work in pure and applied science would be placed before the community and the effectiveness of the Society's influence upon those of the general public who desire to know something of current scientific progress would be increased.

The Council, the report of whose activities you have already heard, has been consistently active in applying itself to the business of the Society, and the members have given your President very helpful and cordial cooperation; to them I wish to tender my sincere thanks. Particularly to the Executive Officers must I express the great indebtedness of the Society and of myself. Professor Elkin, as General Hon. Secretary, has been an unfailing source of guidance and strength, and Dr. Mellor has carried on very thoroughly the exacting and rather thankless task of Hon. Editorial Secretary. He has also diligently addressed himself to the question of increasing the usefulness of the Society by possible increase of the circulation of its journal. Mr. A. Clunies Ross has, as in previous years, exercised a very efficient supervision of all matters connected with the Society's finances, of the satisfactory state of which you have already heard this evening. During the year Mr. H. W. Wood has carried out a considerable amount of much needed work as Hon. Librarian, and to him the Society is thankful.

The Council of 1944 differed in personnel from that in office at the end of 1943 only in respect of the retirement of Dr. G. H. Briggs and Dr. H. S. H. Wardlaw. To these gentlemen I wish to record the Society's appreciation of their valuable service. Dr. Wardlaw was President in 1939.

We offer congratulations to Dr. Ida Brown on having been elected President of the Linnean Society of New South Wales, and to Dr. D. P. Mellor on having attained the degree of Doctor of Science.

In August last Miss Isabel Houison, who had been on the office staff as Assistant Secretary for many years, resigned to carry out a full-time position with the A.N.R.C. For her signal service, marked always by efficiency and the exercise of discretion, I wish on your behalf to express the Society's thanks. We are not unmindful, also, of the efficient carrying out of their many duties by the rest of the clerical staff.

1944 was the year of the triennial award of the Walter Burfitt Prize. There was a large number of entries, and after careful consideration of reports from expert committees, the Council awarded the Medal and Prize to Dr. H. L. Kesteven, M.D., D.Sc., Ch.M., for his distinguished work upon the Osteology, Embryology and Comparative Anatomy of the Vertebrate Head and Neck. It has been one of the many happy events of my year of office to have had the privilege of presenting this prize tonight. I am glad to be able to announce that in order to increase the endowment fund of the Walter Burfitt Prize, Mrs. Walter Burfitt has donated to the Society a sum which brings the total capital to £1,000. This will allow the value of the prize to be increased to £75. The Council is indeed very grateful for this addition to the earlier benefaction from Dr. and Mrs. Burfitt.

The Clarke Memorial Medal, which now is given in rotation within the fields of Geology, Botany and Zoology, was awarded to Professor Agar of Melbourne for his great contribution to the natural science of Australia. The medal was presented at a meeting in May of the Royal Society of Victoria, at which the ex-President, Dr. A. B. Walkom, was present.

On May 30th the Clarke Memorial Lecture was delivered before a large audience by Dr. W. H. Bryan, of the University of Queensland, on the subject " The Relationship of the Australian Continent to the Pacific Ocean, Now and in the Past ".

While considering the Society's activities commemorating Rev. W. B. Clarke, I would like to express great satisfaction that there has recently been published in the Proceedings of the Royal Australian Historical Society a paper by Mr. J. Jervis upon the life and work of Clarke. This paper contains a great deal of documentary information of very great value to all interested in this renowned pioneer geologist and statesman.

Two Liversidge Lectures upon " The Physics of Rubbing Surfaces " were given at the Chemistry School of the University by Dr. Philip Bowden, of the C.S.I.R. Lubrication Research Section (and of Cambridge). These lectures fulfilled adequately the terms of the Liversidge Bequest that such commemorative addresses should embody discussion of current researches.

The affairs of Science House have engaged the close attention of your representatives, one of whom has been Chairman of the Management Committee. The other, Mr. A. R. Penfold, resigned recently on account of his appointment by the Government to investigate developments abroad in the field of plastics. We appreciate Mr. Penfold's long and effective services as a representative on Science House Committee.

As an owner-body we are also considerably indebted to the Hon. Secretary-Treasurer of Science House Management Committee, Dr. N. S. Noble, to whose initiative, discretion and capacity the present very satisfactory state of Science House affairs and the increased revenue to owner-bodies in the last year or two are largely due.

In connection with Science House I am glad to report a recrudescence of interest in the matter of enlarging the present building to provide for the increasing demand for the use of the meeting halls and for permanent rentals of rooms and suites, by scientific and semi-scientific bodies. Taking a long view, it appears probable that a much larger and modernly equipped hall will be required for the scientific activities of this city in the not distant future, and that much increased accommodation will be necessary for those scientific and technical organisations which will desire to conduct their business in an administrative centre devoted mainly to pure and applied science.

The revival of activity concerning extension of Science House was the outcome of a request from our Council and led to the formation of a Science House Extension Committee. This Committee arranged a deputation to the Minister for Local Government which was cordially received. The object of the deputation was to request the Government to consider favourably the possible transfer of the land, west of Science House, to the owner-bodies in the event of a decision to extend.

To Mr. Upton, who is Chairman of the Science House Extension Committee, we, as an owner-body, are grateful for his efforts in this matter.

Professor Priestley was absent on leave from the Council during part of the year in order to attend a Food Conference of the Allied Nations held in Wales. He also visited America and Canada. We congratulate him on the honour of having been nominated by the Commonwealth Government to attend this conference.

Mr. W. H. Maze, a member of Council, was away for three months on leave, during which he accompanied a Western Australian Government expedition to the Kimberley area, and made geographical observations.

In August last the reorganised Oceanography Committee of the A.N.R.C. conducted a two-day conference at the C.S.I.R. Marine Biological Station at Cronulla. This gathering was for the purpose of focussing attention upon oceanographical problems in Australia, and of endeavouring to coordinate work by giving an impetus to the policy of integrating the activities of scattered workers in this field. The conference was distinctly successful and several resolutions were recommended to, and adopted by, the Executive Committee of the Australian National Research Council. These, when implemented, will pave the way for important developments, particularly after the war, in several branches of oceanographical research.

An event of great importance was the appointment by the Commonwealth Government in October last of Professor Eric Ashby as Scientific Attaché to the Australian Legation in Moscow. This appointment was made upon the request and recommendation of the A.N.R.C., and your Council has already expressed its appreciation of the action of the Commonwealth Government in setting up machinery for linking the scientific activities of Australia with those of Russia. Recent information from London records the greatest interest and enthusiasm in governmental and scientific circles there regarding Professor Ashby's mission. In what will be a difficult post we wish Professor Ashby all success, and feel sure that his special gifts will make effective his efforts to provide a channel for the gradual establishment of relationships beneficial to scientific workers in both countries.

The holding of the first U.N.R.R.A. conference at Lapstone, Glenbrook, in November last was an event of national importance. Since much of the activities of U.N.R.R.A. will involve services in the realm of applied science, I am of the opinion that the U.N.R.R.A. organisation should eventually have

affiliated with it some international advisory scientific panel. Such a body could, among other activities, have helpful influence in the broad sphere of international relations.

On March 12th, 1945, your President, accompanied by the Honorary Secretaries, presented at Admiralty House a Loyal Address of Welcome to Their Royal Highnesses the Duke and Duchess of Gloucester. I take much pleasure in reminding you that, as already announced in the Press, the Duke of Gloucester has graciously consented to accept the office of Senior Patron of our Society.

During the year the Council had several requests for evidence of interest in various gatherings or projects sponsored by several organisations, and where considered likely to be fruitful or appropriate some representative of the Council has given his attention to the matter at issue.

The Council was glad to support a move initiated by the Australasian Institute of Mining and Metallurgy for the establishment of a Commonwealth Geological Survey, and a further reference to this matter is made later in my address.

In concluding this part of my address, I recall to you that we have sustained the loss, by the hand of death, of three members.

Dr. Norman Dawson Royle, who died on April 29th, 1944, had been a member since 1929. He was an orthopædic surgeon of international fame. His researches in association with the late Professor John Hunter upon the sympathetic nervation in connection with spastic paralysis were based upon outstanding operative skill and experimental ability, combined with great scientific insight. He gained many honours in the world of medicine and set a very high standard for the award of the Walter Burfitt Prize, of which he was the first recipient in 1929.

Dr. Charles Anderson died on October 25th, 1944, at the age of sixty-eight. He was one of the great servants of our Society, giving abundantly of his rare gifts of scholarship and versatile scientific knowledge, as well as contributing in a unique way to committee activities by the shedding abroad of his own special personal charm. He was President in 1924, Editorial Secretary from 1935 to 1943, and member of Council for 24 years. To other scientific societies he also gave much service, being president and/or councillor of several bodies. Until he turned his attention in later life to vertebrate palæontology, he was essentially a mineralogist, specialising in morphological crystallography. In this field he had a worldwide reputation and his work was highly regarded by that great crystallographer Victor Goldschmidt of Heidelberg.

Sir Thomas Ranken Lyle passed away at the advanced age of eighty-four. He was a distinguished honorary member of the Society, having been elected in 1931. A man of high moral character and strong intellectual attainments, he was a great influence in Australian affairs of science and industry for a long period of time, having been President of the Australian National Research Council, Chairman of the State Electricity Commission of Victoria, and Chairman of the Standards Association of Australia. In his special field of science, physics and mathematics, Lyle's genius was abundantly manifested in outstanding contributions which he made, both in the early part of his career in Ireland, and later while Professor of Natural Philosophy in the University of Melbourne from 1889 to 1915. His distinguished scientific work was recognised by the bestowal of the Fellowship of the Royal Society in 1912, and his unselfish devotion to the best interests of his country led to his being knighted in 1922.

Full obituary notices concerning Dr. Royle, Dr. Anderson and Sir Thomas Lyle have appeared in *The Australian Journal of Science*, Vol. 6, No. 6, and Vol. 7, Nos. 1 and 3.

Part II. SOME RECENT TRENDS IN GEOLOGICAL SCIENCE AND THE EFFECT OF THE WAR ON ITS EXPANDING FRONTIERS.

Scope and Purpose.

The presidential addresses delivered to this Society in the past have been mainly of two types: (*a*) those which summarise existing knowledge in some field of science and perhaps draw attention to advances recently antecedent to the date of the addresses, and (*b*) those which constitute research papers on some specialised work that the retiring President has carried out.

While records of research must in the long run be of more value than digests of existing information, nevertheless, since ours is a general scientific society I have decided upon an address mainly of the former type. This I have done in the hope that it may save the time of geologists (especially younger workers) interested in certain recent developments, and also that the later sections of the address may interest members generally.

An attempt will be made

(i) to trace some trends in geological science just prior to and since the beginning of the war,

(ii) to indicate where war conditions have affected research trends in geology,

(iii) to discuss the general position of geology in relation to war and post-war problems, referring briefly to that of international mineral controls, and

(iv) to make suggestions of possible developments in geological science in the near future.

Since the war has, in general, prevented scientific workers in the Allied countries from having access to publications of enemy countries, and since there has been difficulty in obtaining much information about the details of recent scientific research in Russia, I have, rather arbitrarily, limited my discussion to some of the progress of geological (including mineralogical) science in the two great English-speaking empires. Further, my review deals largely with American research because it has covered the widest fields of earth-science, its extensive development being due to the availability, particularly before America entered the war, of a large number of investigators, often working under the auspices of notable organisations possessing liberal funds.

It is not considered in any way necessary to discuss the lines of Australian geological research in recent years because these are well known to local geologists, and indeed it can be said that because of the limited number of workers available and the impracticability of holding conferences for discussion during the war period, the body of research done here has not been so great as to produce definite trends distinct from those developing abroad.

My remarks are concerned with non-biological aspects of the science, and I will not have time to make more than a passing reference here and there to matters connected with pure igneous and metamorphic petrology.

The Rise of Geophysics in Recent Years, and its Influence on Geological Science.

One great feature of research in earth science during the last twenty years has been the great development of geophysics, and in that wide field the notable

advances bearing directly upon geology have been in the sections of geodesy and seismology. Geology in its modern progress owes much to geophysics and geochemistry, which are more than handmaidens to geology, and in varying degrees are more or less integrated into the whole field of geological science. In fact, geology and geophysics have assisted one another in a great forward march in the last decade.

Geophysical research applied to geological problems has embraced investigations on both large and small scales. The chief contributions on the larger plan have been gravity determinations over land and sea, geophysical contouring of submarine topography and seismological analyses of earth structure. While the geophysical exploration of the land by geodetic methods has for a long time been a normal activity of national organisations in many countries, and particularly in Russia, India, U.S.A. and Germany, the investigation by gravimetric methods of the probable constitution of the sub-oceanic lithosphere may be said to date only from 1923, when Vening Meinesz carried out accurate pendulum observations in a submerged Netherlands submarine while making a voyage from Holland to Java. His later brilliant research feats in this field, carried out mainly in the East Indian and West Indian areas, are regarded by some leading authorities as the most outstanding geophysical achievement in recent years.

Coeval with the spread of geodetic researches in oceanic areas there has developed a remarkable series of bathymetric investigations, the results of which fire the imagination and open up an attractive vista of research for workers interested in the topography of the ocean floor and its implications. I refer to the discovery of submarine canyons on the continental slopes. With the perfecting and extensive use of the Sonic depth-finding apparatus, invented about 1923, there is now available a vast amount of data, committed to paper in articles and maps, concerning the detailed submarine topography of portions of the lithospheric surface constituting the continental shelf and the continental slope. In addition much information as to the general floor configuration of many deep oceanic areas is known.

The submarine canyons on the continental slope have provided many challenging and subtle problems—problems which lead us into the realm of fundamental structural geology of the continental borders and the sub-oceanic crust. The development of the Sonic sounding method may be looked upon as epochal in its contribution to studies of the ocean floor. Some people regard this method as having given an impetus in the study of submarine geology comparable in importance to the effect of the invention of the polarising microscope upon petrography, or to the effect of experimental analysis of mineral phase systems upon physico-chemical petrology.

The combined information from sonic sounding, gravity measurements at sea and on land, and from earthquake analysis gives a background for discussing the evolution of continental borders and island arcs (the regions of great instability) and the character and structure of the crust under the oceans. It thus throws light upon controversies centring around the theories of permanence or impermanence of oceans and continental blocks.

The whole convergence of geophysical evidence concerning the crust below the continental surface, beneath the submerged continental borders, and beneath the true oceanic segments may therefore be applied to vital purely geological problems, for it has long been recognised that the constitution and changing condition of crustal materials have largely determined the operation of many fundamental processes.

As examples of this dependence we may note

(*a*) In Petrology the ultimate problem is the origin of magmas.

(*b*) In Economic Geology the nature and origin of the ore-fluids and the vicissitudes through which they pass before depositing ores are topics that lead back to the subterranean environment whence these fluids were derived, and to the study of the fracture systems available for their wanderings.

(*c*) In Structural Geology no rational basis of tectonic evolution can be erected without some fixed ideas as to the behaviour of subcrustal material.

(*d*) In Vulcanology the setting for most problems is a geophysical one.

(*e*) In Metamorphic Geology the progressive changes wrought by magma fluids and stresses can be satisfactorily essayed only in the light of a theory concerning the major adjustments of the crust.

(*f*) In the study of Physiography diastrophic controls have a major importance, and these lead back to the proximate causes of these controls.

In references to recent geophysical research I will not be dealing with those specific technical advances in geophysical exploration and prospecting for commercial deposits of fuels and metallic ores—a subject of great importance. Rather we shall consider purely academic investigations. Nevertheless it should be pointed out that the activities of commercial organisations making seismic and other investigations have had an immense effect on academic studies in the same fields.

Much that has been achieved is due to the splendid coordination of work in scientific institutions, often very well endowed, and government services, especially the navies of Britain, America and Holland. Such coordination owes much to cooperation inspired and painstakingly worked out by scientists of many countries (particularly of Russia, Britain, America and Holland), who have functioned through the International Union of Geodesy and Geophysics, through the International Geological and other Congresses, and especially within the framework of the vigorous American Geophysical Union, which is the American Committee of the International Union. This body has, by excellent organisation of its many subsections, brought about a great nation-wide stock-taking in many spheres of research-endeavour by the holding of conferences and symposia. The spheres that interest us here are the divisions of Oceanography, Geodesy and the newly erected section of Tectonophysics, which embraces special aspects of structural geology, including the experimental approach, in which physical principles are fully allowed for.

The insistent demand, in recent decades, for a broad theory concerning the structure and physical condition of the earth, especially in its crustal portions, generated a great urge for integration of a wide series of researches, experimental and otherwise, which had been conducted all over the world. This urge has found expression and response in the cooperation of specialists to attack major problems in earth-science over a period of years. Accordingly many active committees in geophysics have been set up, some of which have become international in scope and personnel. In all this teamwork several men of the highest calibre of research genius have stood out as inspiring leaders. Such names as those of Bridgman, Birch, Vening Meinesz, Nikiforov, Ewing, O. T. Jones, Bullard, Bowie, Macelwane, Jeffreys, Gutenberg and R. A. Daly come to one's mind. The last-mentioned has achieved the greatest success in promoting a convergence of experimental evidence upon the subject of the strength, constitution and tectonic evolution of the earth's outermost shells. Of him, the

distinguished President of Harvard University, Dr. Conant, recently said: " A geologist of rare imagination and wide vision, his enthusiasm has aroused physicists, chemists and astronomers to cooperate in the advancement of his science."

It would seem that the challenge provided by the oceans, and the crustal materials forming their floors, could only be adequately met by *international* research activities, and thus the gradual shifting of emphasis in geological-geophysical research from that upon continental geology to that upon submarine geology is largely a fruit of the breaking-down of national barriers in science.

We may now proceed to note some advances in the geophysical attack on geological problems.

Two very important books of fairly recent date, viz. Daly's " Strength and Structure of the Earth " (1940) and " The Internal Constitution of the Earth " edited by Gutenberg (1939), cover most of the fields of geological-geophysical research up to 1939. There is thus no need to specify the results of work detailed in these excellent publications, but some more recent results in the present field, and some, less recent but not discussed in the books cited, will be briefly considered below. In view of the importance, in the writer's opinion, of geodetic approach to structural-geological research, most notice will be taken of trends in that section. Some years ago it appeared that seismic tests to determine structure might become more widely used, but for academic geological purposes it appears that, at least in America, gravimetric work has taken precedence.

Concerning submarine topography on the slopes it will not be necessary to repeat the detail of advances given in such readable works as the recent publications by Johnson (1940) and Veatch and Smith (1939).

Research upon Gravity Anomalies in Relation to Geological Structure of Continents.

General.

Some of the chief activities of geophysicists in recent years have centred around the geological interpretation of gravity anomalies in areas lacking isostatic equilibrium.

The corollaries of the existence of such anomalies (whatever particular kind may be calculated according to the accepted theory of the figure of the earth) relate to the constitution, strength and tectonic history of the lithospheric materials. The belief that differences in density of the underlying materials caused the anomalies was the starting point in these studies, and since the evaluation of gravity anomalies as indices of geological peculiarities below the continental surface is a matter of great importance, we shall note some leading types of work recently accomplished.

Excellent researches upon East Africa, India, Finland and Siberia, as well as in America and elsewhere, have been conducted in the last fifteen years, and of these Bullard's study (1936) on the Rift Valleys of East Africa is one of the most outstanding in indicating the relation of local gravity anomaly values to the geological structure and tectonic condition.

The work of Chamberlin (1935) in the Beartooth-Bighorn Mountains was noteworthy as he introduced the principle of correcting the anomaly-value by applying a geological factor based on composition of terrain.

Recent Work in U.S.A.

A leading principle in this comparative study of gravity data and geological data in the United States is the recognition of the part played by the Basement Complex (ancient, rigidly compacted and mostly metamorphosed) which underlies the less compacted sediments of so many areas, or is exposed elsewhere.

The Basement Complex of U.S.A., by virtue of its greater density, will be reflected in the existence of gravity anomalies in regions mantled by uniform sediments.

This crystalline basement of North America has had a great influence in the geological evolution of U.S.A., and the interests of geologists in its position and structural condition has led to the preparation, by a committee of the American Geophysical Union, of a structure-contour map of the surface, as occurring in most of U.S.A. A comparison between this map (published 1938) and the gravity anomaly map of the U.S.A. shows a remarkable degree of accordance between geology and gravity distribution. In general, also, the map indicates that various areas of pronounced seismicity correspond with special structural features in the Basement, known or inferred.

In recent years attempts have been made to trace the Basement's tectonic and petrological evolution. It can be noted that there are characters about it which are not met with in later terrains. Thus while we are apt to expect localised folded tracts with associated batholithic intrusives to be characteristic of post-pre-Cambrian provinces, we do not find such restricted diastrophism and magmatic activity in the Basement Complex. On the other hand, there is evidence of widespread intense deformation and igneous injection over vast areas, especially in Archæan regions.

It is clear that in pre-Cambrian time extensive metamorphism was due to the existence of high isogeotherms in the crust. Successive foldings and injections of mainly granitic material were possible because of the greater mobility of the sialic crust, which was relatively thin.

The special implications of the Basement Complex regarding the constitution of the earth's interior, particularly the composition of the upper shells in pre-Cambrian time, have led to the hypothesis, recently put forward by Buddington (1939) to account for the occurrence of large anorthositic masses of the Adirondack type. These masses are distinguished from the differing, sheet-like anorthosites, and are confined to the pre-Cambrian. Buddington suggests the great domical anorthositic intrusives were parts of a significant primitive layer in the zoned crust, which came into existence in the primal gravitative settling during crystallisation of the molten earth. The extreme temperatures of early pre-Cambrian time would thus allow the melting of the anorthosite layer, and the emplacement of monomineralic intrusions within the uppermost crust of that period. The limited occurrence of this type of layer and the lower values for the crustal isogeotherms since pre-Cambrian time are envisaged as preventing the later development of anorthositic magmas. Recently a paper by Harrison (1944) gives field evidence from the Ontario anorthosites which lends some support to Buddington's view.

A study of the basement map leads to the recognition of many areas suitable for treatment by intensive investigations concerning (*a*) gravity anomalies, and (*b*) seismic reaction.

Under (*a*) we note a series of studies by G. P. Woollard (see References), who has examined the distribution of gravity anomalies of U.S.A. as a whole, and also has concentrated upon certain test areas in particular.

In his earlier general work (1936-39) he dealt with the following principal factors causing gravity anomalies :

(*a*) Density-variation in the surface rocks.

(*b*) Surface position and deeper structures of the Basement Complex.

(*c*) Structure of the basic stratum below the Basement.

(*d*) The degree of isostatic equilibrium in the locality examined.

As a result of extensive geophysical work in eastern U.S.A. (first, siesmic work in collaboration with Ewing and others (1939) and later gravimetric work),

Woollard (1940) came to an important conclusion, (*a*) below, and indicated a very interesting probable structural relationship, (*b*) below :

(*a*) Along the eastern American seaboard there appears to be a genetic relationship between the distribution of the gravity-strips and the Appalachian Chains, since they are broadly parallel in all geological provinces of the region.

(*b*) In one part of the Piedmont (the ancient crystallines thrust against the folded Appalachian tract) a remarkable inference may be drawn from the existence of a gravity-trough which reveals a probable buried tectogene (in the sense of Hess (1938)).

In his Virginia studies Woollard used the gravity-map, the basement structure-map and the geology-map in association, and demonstrated the following chief interrelations between gravity and geology :

(*a*) A mass-density distribution which varies with the lithological changes.

(*b*) An absence of isostatic equilibrium due to some fundamental change in the character of the basement rock-type.

Woollard (1943) surpassed all his previous achievements in geophysical-geological field studies by his great transcontinental gravity and magnetic traverse across the United States from the Californian coast to New Jersey on the east.

In a most thorough investigation of the relations of regional and local gravitational and magnetic data, Woollard has shown that in the east, control in the magnetic and gravity phenomena was exercised by lithological changes in the Basement Complex rather than density values in the rocks above the Basement. In the west, however, density-variations in supra-basement rocks, and contrast between the density of these rocks and the basement, were the controls. Large regional (residual) anomalies were clearly due to deep-seated causes.

Woollard (1943*a*) carried out a further intensive study of the New Jersey area which had received some attention in the larger traverse. He found that all the main anomaly zones were parallel to the Appalachian Chains, and that the underlying basement controlled the marked local anomaly distribution more than did structure, lithology and thickness of the overlying sediments. Further, deep-seated lithological variation produced large regional anomalies.

Woollard has stressed the importance of carrying out magnetic as well as gravitational surveys and concentrating upon local areas with significant features, after the regional effects have been evaluated.

Longwell's gravity investigations in eastern U.S.A. (1943) represent a first-class analysis of the geology-gravity relationship. He finds that the anomalies in the region have features of two kinds :

(*a*) those revealing a regional element not connected with the surface geology,

(*b*) those reflecting surface rock-masses with abnormal densities.

Isoanomaly maps for " isostatic ", Bouguer and free-air anomalies indicate the existence of pronounced gravity troughs of negative values with a notable positive strip between them. These can be correlated thus—areas of sedimentation and strong folding lie along the sites of the negative strips, while an uplifted area is along the positive belt. This work gives a really satisfactory correspondence between geological structure and history on the one hand and anomaly-variation on the other. It has been confirmed in regard to one strip of negative anomalies by Ruedemann's (1944) account of the Hudson Valley deep graptolite zones which imply a downward bulge of the sial.

The investigations of Hersey (1944) in Pennsylvania indicate the method of correlation between geology and gravity-data where both regional and local variations in anomalies exist. He found the local anomalies were connected with Appalachian structural trends delineated by contrasted outcropping rocks. This paper indicates the possible usefulness of such studies in a region of diverse lithology.

Some Gravity Studies in Other Countries.

D. C. Skeels (1940) has given some attention to the question of the gravity-conditions of sedimentary basins in various parts of the world. Since the present unfolded or broadly warped sedimentary troughs contain masses that are less dense than the surrounding and underlying basement rocks, it would be expected that minimal gravity values would be registered in regions characterised by extended geosynclinal prisms lying within old terrains.

Evidence showed that in Italy the deficiency-distribution in the Po Valley Tertiary Basin of sediments was such as to lead one to infer that the Appennines had been thrust over part of the basin, whose central gravity-trough probably lies some distance under the Appennine Thrust Sheet.

In India the gravity anomaly map shows, at first sight, little sympathy with the geological make-up. This may be due to the prevalence of igneous pre-Cambrian rocks. But in one district there is a notable exception. This is due to the existence of the Cuddapah Basin, composed of ancient sediments which, strangely enough, happen to have mass-density greater than that of the surrounding platform. The gravity minimum is found superimposed on the basin-structural-plan. Skeels suggests that the deficiency must therefore be due to the down-warping of the sediments and the granitic layer into the basic substratum. This recalls the down-warped area of the western Appalachian Chain mentioned above.

Geophysical Research on Continental Borders and Marine Areas.

A great deal of interest has surrounded the determination by seismic and gravity measurements (largely given momentum by investigations of oil companies) upon the disposition of the pre-Cretaceous Appalachian surface that underlies the sediments of the Coastal Plain. Ewing (1939) has been active in the work of tracing the basement-surface out into the Atlantic Ocean. The geophysical work along the Gulf Coast has also been of outstanding importance.

From many lines of evidence a great deal is known about the evolution of the Appalachian surface throughout post-Cambrian time, and geophysical work has now revealed the extension of this surface well out into the Atlantic. The evidence of the submarine canyons supports this result. It is remarkable to note that up to 10,000 feet of sediment has been measured resting on the basement at a zone 40 miles from the coast.

A similar extension seaward beyond the continental shelf of the Palæozoic platform of southern England has been demonstrated by the excellent work of Bullard and Gaskell (1938). They have, by the " Seismic Refraction " method, determined the existence of at least 4,000 feet of sediment on the shelf nearly 200 miles south-west of The Lizard. It is clear that there is an urgent need for more geodetic determinations in the Atlantic area between these two zones of sialic extensions. W. H. Bucher (1940) has taken up this problem and indicated the possibility of a general tectonic or physical behaviour of the Atlantic floor not unlike that shown by continental surfaces which have bulged and fractured. This leads to the problem of deciding how much of the sub-Atlantic surface is sialic. Another body of evidence impinging on this subject is that derived from

the investigation of the floor of the Indian Ocean by the John Murray Expedition of 1934 (see Wiseman and Sewell, 1937). Geodetic measurements, sampling of the rocks of the floor, and echo-sounding over 22,000 miles in the Arabian Sea and North Indian Ocean gave data indicating the presence of discontinuous slabs of sialic material resting on basic substratum.

Further light on this problem comes from J. T. Wilson's recent analyses of seismograms of a large earthquake originating in the South Atlantic. He concluded that the average bedrock type of the Pacific and of the Atlantic are similar. This would be in harmony with the existence of separate and subordinate sialic patches on the floor of the Atlantic and of the South-west Pacific.

The foregoing considerations have some bearing on the Wegener Theory, and one might make a digression here to note a recrudescence of interest in and a renewal of controversy about the Wegener Theory during the last few years. This was prompted by the appearance of a paper by Simpson (1943) dealing with the distribution of mammals in both hemispheres. Simpson opposes the Drift Theory and supports that of Stable Continents. This paper drew forth a vigorous reply from Du Toit (1944), the great protagonist of the Wegener Displacement Theory. Bailey Willis (1944) entered the discussion to describe the Wegener Theory as a " fairy-tale " and C. R. Longwell (1944) gave a very balanced and mostly non-committal statement about the new minor controversy.

Some Laboratory Geophysical Investigations.

The epoch-making series of geophysical experiments carried out at Harvard since 1934 mainly in the laboratories directed by Prof. Bridgman are well known. They constitute one of the most pronounced trends in applications of geophysical experiments to vital problems in geology. It was natural that these researches should develop at Harvard, since Daly had for many years required to know how valid were his assumptions about the nature of the asthenosphere. For several years prior to 1938 he had been moving towards the hypothesis of an earth model in which the strong upper sialic crust rested on a crystallised gabbroic layer, which in turn rested on a weak, hot and vitreous substratum, in the existence of which could be found an explanation for so much of the geological behaviour of continents.

P. W. Bridgman, a world-famed specialist in high-pressure technique, had perfected apparatus with which tests upon rock materials could be conducted. The result of cooperation between the Bridgman school and the geologists has given to the scientific world a set of unimpeachable data from experiments carried out by brilliant workers. The chief investigators have been (in addition to Bridgman) Birch, D. Bancroft, Dow, Ide and Griggs. Griggs (a geologist who is also a trained physicist) has specialised in the geological applications of his high-pressure work.

The experiments have been mainly in two categories :

(*a*) Those which have been conducted to determine various physical properties such as

- (i) thermal conductivity of rocks and its relation to composition ;
- (ii) rigidity and compressibility of rock-types at room temperature and at elevated temperatures ;
- (iii) the effect of pressure on rigidity.

(Such experiments help to discover the values of seismic velocities in certain rocks assuming their existence at various depths of the lithosphere.)

(*b*) Those which investigate the behaviour of rocks under high confining pressures, at normal and at elevated temperatures. In this category Griggs has developed technique whereby the following five factors can be achieved simultaneously :

(i) High confining pressures.
(ii) Shear stress.
(iii) Elevated temperature.
(iv) Presence of solutions.
(v) Considerable time-interval.

(Such experiments are calculated to investigate the probable rôles of plastic deformation and rupture in rocks under such conditions, and point the way of experimental approach to the study of dynamic metamorphism.)

The latest contribution to this field of work has been the research by Birch and D. Bancroft (1942) on the effect of temperature upon the elastic properties of glasses (including artificial basalt-glass). The results of this work give food for thought.

Elasticity and internal friction have been examined up to a temperature of 600° C. and the relations of viscosity, rigidity and internal friction studied. The effect of pressure on the behaviour of the glasses has also been estimated.

These physicists, after considering all the data, have decided that the velocities that could be transmitted by an earth-layer of basalt-glass in the position, and at the temperature postulated for the vitreous substratum, would be considerably less than the velocities known by seismologists to have characterised the passage of earth waves through the material in the earth at a depth of 60 Km.

It is not too much to say that the experiments noted will rank as one of the greatest impetuses in this century in the development of fundamental research in geology.

(Leading references to this section are grouped in the Bibliography.)

In summary, therefore, we note that four important trends in combined geological-geophysical researches have developed in the last decade. These are

(*a*) investigations of continental areas by gravity, magnetic and seismic traverses leading to an interpretation of the geological structure, lithology and tectonic history, especially the relation between the near-surface rocks and those of the older basement terrains ;

(*b*) the measurement of gravity at sea and the interpretation of the lithology and tectonic condition of the sub-oceanic crust.

(*c*) the determination of submarine topography by echo-sounding on a large scale, leading to results that have called forth an important series of discussions of fundamental physical geology ;

(*d*) laboratory investigation upon the physical behaviour of rock materials at high temperatures, high pressures, and in the presence of liquids, over considerable periods of time. This has been done in order to compare satisfactorily the physical condition postulated for the upper shells of the earth with that revealed by seismographic and other analyses of the passage of earth waves.

(No discussion of purely seismological attack on the problem of earth-constitution is given here, since this aspect, while very important, does not represent a recent trend in geophysical geology.)

A Plea for a School of Geophysics in Australia.

In view of the importance of geophysics in connection with so many phases of geological research, it is to be deplored that Australia is unable to pursue adequately the type of work that is marking many of the leading research projects tackled by scientists abroad. But while pure academic coordination of geological and geophysical work is eminently desirable, it is to be stressed that modern development of our mineral and fuel resources needs geophysical aid as an extra weapon to geological exploration. Some excellent pioneering work has been done in Australia, particularly by the officers of the Mineral Resources Survey, and formerly by other government geological branches, but what is needed is a School of Geophysics in Australia, so that broadly trained graduates may be available for the work that will soon be urgent if this country is to take a worthy place in future national and international development.

In his presidential address to this Society in 1937, Dr. Booth made a concluding statement about the absence of a Chair of Geophysics in any Australian University ; this amounted to a plea for such a Chair, and I wish to reiterate this tonight. Such a School of Geophysics, by virtue of the coordinating help from other departments, could train graduates who, according to their background and inclinations, would be able to specialise in different sections of the science.

There are, of course, many fields of geophysical work apart from those of interest to pure and applied geology, and some excellent work is being carried out in one or two of these, but other fields are untouched and there is no source of trained personnel. The longer the delay, the more herculean will be the task of the pioneers.

It may be remarked here that in connection with the development of geological oceanography in Australia there has been evidence of more than academic interest from authorities in the British Navy and from governmental and university authorities in America in the possible project of a geophysical survey of the east coast, and especially the Barrier Reef area, of Australia. Such would give a great deal of information regarding the submarine topography, structure and constitution of this region, information that would form the starting point for most of the other oceanographical considerations in this region. It must be seen to that the interest of other countries is not allowed to wane because of inaction here.

In America much care is taken in the formulation of university and college curricula covering the training of geophysicists. Some years ago, for example, conferences were held in which one of the chief items of discussion was the attainment of a perspective in schemes of teaching and research within the field of geophysics, especially as applicable to geological problems. Several publications have dealt with this matter (see Kelly, 1938 ; Hubbert, 1938 ; Heiland and Wantland, 1938 ; Keys, 1938 ; and Barton, 1938).

Some Trends in Structural Geology.

Researches in structural geology have developed greatly in the last seven or eight years, and many advances have been made. A good deal of interest has been shown in structural studies as a distinct field of work, rather than as a section always to be incorporated into more comprehensive researches.

One significant feature concerning this branch of geology is the relatively large number of textbooks and monographs on this subject that have appeared in the last five years, either as new publications or as noticeably modernised editions of well-known texts. It is disappointing to have to record that the only structural geology textbook emanating from Britain in this period is one that does not measure up to the scope of fundamental advances that have occurred in the subject. This is the fifth edition of James Geikie's book (edited by Craig

and Campbell), which, while sound and satisfying in the matter of descriptive treatment, takes little note of the wide literature dealing with the genetic side of structural geology, nor presents the student with a perspective for evaluating the relative importance of various structures in regard to tectonic evolution of a region.

On the other hand, the new editions of Nevin and Lahee and the new books by Billings (1942) and Hills (1940) present structural geology in all its modern outlook and emphasise the genetic side of structures and the applications of physical laws in the study of the behaviour of rocks during deformation.

Of the books cited, that by Billings appears (from reviews) to be one of the most important texts yet published on structural geology, while the little book by Prof. E. S. Hills, of Melbourne, is likely to prove the most useful for intermediate and senior folk who, in a busy era, require an up to date, comprehensive and balanced treatment of a very wide, and in part difficult, branch of geology. In addition to these textbooks two important works have appeared since 1937. These are Balk (1937), "The Structural Behaviour of Igneous Rocks", and Anderson (1942) on the "Dynamics of Faulting and Dyke Formation", in the latter of which an analytical treatment is presented.

All these publications on structural geology may be said to be a sure guide to trends developing in the subject, for they reflect the major interests that are being shown by workers in several branches of tectonics. These interests arise from two main factors:

(i) the demands, direct and indirect, of economic geology in connection with structural control of ore deposition and oil and gas accumulation;

(ii) the gradual evolution of the subject, largely instigated by the influence of leaders in both field and laboratory studies.

A very important trend in the past decade which has become even more marked in recent years is the interest and increased attention to the internal structures of igneous rocks, as distinct from structures that have developed by deformation subsequent to their consolidation. The great advances in this section have been grounded largely on the epoch-making contribution of Hans Cloos in his experiments and field studies on flow structures and fractures in igneous rocks and related matters. The essence of these studies is that the evidence of flowage combined with a study of syngenetic fractures must give a basis for interpreting the history of movement of the mass, i.e. its ascent, migration and emplacement on the one hand, or its extrusive history on the other (according as it be intrusive or volcanic in nature). Such tectonic analyses give a clue regarding the forces acting during the interval from intrusion to final crystallisation. Such information provides part of the tectonic history of the whole region where extensive igneous rocks occur. The later deformations that may affect igneous and associated country rock alike have then to be worked out from a regional tectonic analysis by the elucidation of interrelated structural data.

In the structural study of flowage features much can be done megascopically, but it is clear that, apart from field analyses of linear and platy structures, microscopic investigations will play a part, and petrofabric analysis may be the dominant contribution to a solution of a problem. (Reference to petrofabrics is made below.)

The influence of Hans Cloos, especially in American studies, has been extended by leading workers, chief amongst whom are Ernst Cloos, Balk, and Evans Mayo.

It is now becoming the usual procedure to express the results of structural analyses of igneous masses (especially intrusive bodies) by tectonic maps. Many of these are most complicated, but by sifting the evidence one may use the

various structure patterns presented with considerable success. These maps are helpful in dealing with such matters as mechanics of injection, regional tectonics in relation to eruptivity, and metamorphism in relation to igneous action.

In structural studies upon regionally deformed sedimentary and volcanic terrains a great deal of attention has, in recent years, been paid to the fracture patterns. Here the genetic aspect of folds, of faults and joints and other varieties of fractures has been the dominant interest. Workers have been forced to realise that a rational physical basis for the fracturing of rocks must be sought, and if possible established, before a satisfactory tectonic synthesis can be achieved.

In the field of economic geology the cardinal principle of the structural control of movements of ore fluids and of ore-deposition has been much more widely recognised. This has been vividly manifested in a large percentage of the extensive series of recent papers. Careful systematic plotting and analysis of fracture-patterns have in many cases provided the rationale of theories involving prediction of ore-reserves.

The growing interest in the relation between the type of rock deformation and the resulting fracture-pattern is also reflected in the relative space allotted in recent textbooks to the subject of " Structural Control ". This is particularly the case in the latest edition of Emmons (1940) and in Bateman's excellent new text (1944).

Thus we have clear evidence of a dominant trend in the work of structural geologists expressing itself in a determination to arrive at as complete a picture of the dynamic history of a region investigated as is possible.

In connection with recent studies in England one is struck with the thoroughness with which these have been conducted. Many investigations, frequently in small areas, have been directed to elucidating the intimacies of related folding and faulting in sedimentary terrains that have been subjected to fairly localised stress distribution. A vogue that has arisen in England is the employment of a hand-auger, to give, in quick fashion, information not available at the surface. The work of Arkell (1943-44) and George (1940) may be cited as among the most recent contributions. One cannot help qualifying the recent structural work in England by quoting a sentence noted in recent geological reading :

> " As a rule very careful and detailed study of a small region furnishes results more useful to others than the most brilliant generalisations based on insecure facts. Unfortunately, detailed work is time-consuming and not very inspiring, whereas the large picture is more spectacular and also more interesting."

However, the larger picture may give a perspective in megatectonics and help to place a local problem in its correct setting. Thus we note that there have been some important contributions to literature by British and American workers which deal with regional problems.

We shall now note some of the more important recent advances. M. P. Billings, of Harvard, and many of his students have described the structural geology and metamorphism of the New Hampshire and neighbouring regions in a series of splendid papers. The importance of structural control of magmatic activity is the keynote to many of these studies. The delineation of the structure in the folded terrains is accomplished largely by paying great attention to small-scale features such as fracture-cleavage, drag-folds and the variations of " pitch ". Arising out of these researches has come the recognition of several ring-dyke complexes which differ in some aspects from the British Tertiary Ring Complexes.

Billings' experience in these areas has coloured the treatment of his recent book, as he has given considerable notice to the structural aspects of igneous rocks.

What has been described as " the most intensive structural investigation of a considerable area that has yet been carried out in America " is the brilliant research dealing with the " Martic Overthrust " by Ernst Cloos and Anna Hietanen (1941). This deals with the region between New Jersey and Alabama, where fundamental problems (chiefly structural) of Appalachian and Basement geology have been elucidated by every known means of structural and petrological (including petrofabric) analysis. The synthesis of the tectonic history, based upon the coordination of tectonic maps, petrofabric results and the study of metamorphic evolution, is an outstanding piece of work which all structural geologists should read.

An interesting development, possibly partly due to the war, has been the preparation and publication of several important papers by leading economic geologists and active or retired Colonial officers, some of whom, because of war conditions, have gravitated back to their central offices in London and elsewhere. A further factor in the appearance of these papers has been the appeal for contributions by editors of geological journals which have suffered a diminution in the number of research papers coming from the ordinary sources because of the war.

Several structural papers upon regions in Asia Minor and in various territories administered by the Colonial Office are worthy of attention. In most of these, regional fold-systems have been examined in relation to associated faults. A valuable contribution to tectonic geology is the publication by Busk (1939) of a beautiful block-diagram showing part of the Rift Valley of East Africa.

Concerning structural aspects of the pre-Cambrian, we note the important paper by D. R. Derry (1939) in which he shows by careful mapping that the roots of the early pre-Cambrian folds of Canada contain simpler structures on the whole than, for example, those usually found in the upper parts of a great folded mountain complex. Great lateral thrusts and recumbent structures are absent, and steeply dipping metasedimentary rocks and associated igneous masses are prevalent, separated by steep thrust faults. These associated features suggest that groups of nappes in an orogen must gradually merge downwards, by a reversal of the thrust-fault dispositions, into such root-structures as seen in this province. This is a significant paper giving evidence of a renewed trend of thought about pre-Cambrian systems, and it recalls similar views by Swiss geologists for certain Alpine root structures.

In the field of megatectonics, some recent evidence from India, chiefly due to W. D. West (1935, 1939), indicates the presence of great overthrusting, with the production of nappes and windows, in parts of the Himalayas, and the presence of recumbent folds in the metamorphic rocks of the Nagpur area of Peninsular India. The detailed evidence given in geological literature about similar structures, together with this new Indian information, suggests that overfolding, extensive thrusting and excessive granitic invasions are a feature of the ancient metamorphic terrains of the world.

The trend of investigations in this field has been towards establishing the existence of the overfolds by detailed stratigraphic observations coupled with such structural evidences as graded and current bedding in arenaceous rocks. As the solution of many pre-Cambrian problems will ultimately be sought in the study of metamorphic response during tectonic evolution, it is good to note, from recent literature, that several workers interested in the megatectonics of metamorphic regions are seeking the aid of petrofabric analyses of small-scale structures.

An important piece of collaborative work has recently been completed in the compilation of a tectonic map of U.S.A. This has been done under the auspices of a National Research Council Committee headed by C. R. Longwell (1944). This map, on which many varied tectonic features are delineated, will, in conjunction with other regional maps, such as the areal geological map of U.S.A. and the Basement Structure-Contour Map, provide a groundwork for many structural studies, especially those in the field of comparative tectonics.

Comparative tectonics had been a great feature of European researches in a previous generation, and a trend towards this fruitful line of study is seen in the results of the work, carried out some years ago by the pre-Cambrian Committee, which embraced specialists from Scandinavia, England and America. A later evidence of this trend is the interest of many structural geologists in the conception of Tectonic Provinces.

From a review of the whole field of structural-geological researches during the last few years one important fact emerges. This is, that there is a very urgent need for the establishment of an international committee to overhaul the nomenclature of structural geology, especially in regard to such terms as folding, flowage, flow-cleavage, fracture-cleavage, schistosity, foliation and so on. Greater precision of definition (based on genetic considerations) and keener discrimination regarding the rôle of any feature are needed.

In this connection one cites the recent work of Turner (1942), which shows a deep realisation of the whole problem of the interrelated aspects of many structural entities like cleavage and schistosity.

Again, the whole subject of "faulting" needs clarifying from the point of view of terminology, and here an international committee could do good work. The arbitrary and rather loose use of terms in connection with "faults" leads to confusion, especially among students. Further, one must plead for a more exact phraseology and more careful use of terms in the textbook discussions of the forces operative in crustal deformation. Terms used (especially relating to the many kinds of stress) should be properly defined and consistently employed.

Finally, it is good to note the definite tendency of structural geologists towards a clearer recognition of the limited application of the strain ellipsoid to geological problems. Hills' (1940, p. 24) conception of a "form ellipsoid" in this connection is a very helpful one.

Experimental Structural Research.

In a previous section of this address I referred to certain physical experiments which had been explicitly designed to aid geological science. These experiments, however, were for the purpose of throwing light upon the fundamental properties and behaviour of the crustal layers rather than for illuminating some purely geological field-problem where surface mapping and resulting interpretation are the main factors.

Experiments for aiding such structural field research have generally involved the construction and deformation of models. In these models substances such as clay, wax, plaster, rubber and the like have been used to represent rock units. The behaviour of the materials as a result of the applications of stresses has then been studied and interpreted in the direction of throwing light upon the dynamics of earth movements.

Of the considerable amount of experimental structural work that has been attempted, some experiments gave an approach to simulating actual dynamic conditions of nature, but the majority were conducted on the most insecure and unsound premises. The great fault lay in the fact that the materials employed to represent rocks were much too strong considering the scale-factor, and generally the condition of confinement of the materials rendered the experiments futile. In particular the folding of the "artificial rocks" was generally accomplished

upon a rigid " floor ". With the exception of certain experiments, notable amongst which were those of Cloos (1930), Kuenen (1936) and Summers (1932), work prior to 1937 (including the so-called classical studies of Bailey Willis) had little value.

However, in 1937 there appeared an epochal paper by M. K. Hubbert (1937) that was to revolutionise the whole outlook upon experimental tectonics. In this paper Hubbert shows convincingly the need for dimensional analysis in setting up an experiment to simulate geological deformation. In other words the model must be scaled down so as to be dynamically similar to the original (the earth). The very important aspect of comparative " strength " of model and original enters into the analysis. Thus for small models dealing with building of mountains such substances as wax, grease, sawdust and oil, almost liquid clay and the like have to be employed as the " rocks ". Hubbert gave in his paper some instructive examples of the method of computing scale-model factors. The effect of this paper in geological circles has been notable and workers in several countries have adapted their experiments to the correct principles.

Chief amongst those who have done recent experimental work on tectonics is D. T. Griggs, already referred to in regard to high-pressure work. Griggs (1939) set out to produce folded mountain chains by building a scale model of a plastic crust on a fluid substratum, which would then be deformed by a very ingenious mechanism simulating the action of downward-moving convection currents.

To appreciate Griggs's experiment we must turn to another trend in tectonic geology. This is the mountain building theory of Hess and all that lies behind it. Hess bases his hypothesis on the results of the brilliant and arduous work in gravity measurements and submarine contouring which he and Vening Meinesz and associated workers have done in the West Indies.

Now well known to all geologists are the details of Meinesz' gravity-anomaly discoveries in the East and West Indies (1934). The negative anomaly-strips lie along zones of the down-warped crust where the sial is thickened by displacing sima, which may flow away laterally. Vening Meinesz took the view that the causes of the downward bulge are due to vertically descending convection currents in the sima. These draw down the " skin " of a sialic segment and cause folding of the overlying laterally-thrust sediments which have accumulated in an original geosynclinal depression.

Starting with these conceptions Hess (1938) has envisaged the following sequence of diastrophic events in a region like the West Indies :

(i) Formation of tectogene (or deep) by downward bulge with concomitant upward squeezing of any sediments present.

During this movement the peridotite layer of the crust is tapped to form belt-like intrusions (later to be serpentinised) which are a feature of alpine fold chains in many parts of the world.

(ii) Emergence of geanticlinal borders of tectogene and development of volcanics on one side of tectogene.

Erosion of geanticlines and filling of geotectocline (i.e. great basin of geosynclinal development).

(iii) Second great deformation which folds very intensely the sediments in the geotectocline thus giving orogenic tracts.

Hess' theory developed from his special work in the West Indies, and from a consideration of the modern implications of Kuenen's (1936) experiments. Kuenen, a brilliant Dutch structural geologist, carried out experiments on geosynclinal development, with scale-models which had the advantage of employing a very yielding substratum, which represented the asthenosphere, although exact dynamical similarity was not achieved.

D. T. Griggs (1939) followed up Hess' extensions of Meinesz' and Kuenen's ideas, and carried out the most ingenious tectonic experiments yet devised. Pointing out that Kuenen's substratum (which was water or oil) did not exert enough viscous resistance to the moving overlying sialic layer, he proceeded to build a dynamically similar scale-model of a geosynclinal tract possessing sediments overlying a weak substratum.

The " sima " of the experiment was made of viscous waterglass, and the continental material was made from various mixtures of oil and sawdust. Two rotating drums, driven electrically, were available in the waterglass. These could be revolved separately or together so as to simulate thermal convection currents. By operating both drums Griggs obtained a symmetrical folded tract with border-thrusts recalling Kober's scheme. By operating one drum he obtained a one-sided orogen with strong border-thrusts.

Griggs thus developed a convection-current theory of mountain building based on the principles of Hess' postulated tectogene, and he went further to apply the theory to world tectonics. The importance of Griggs' experiments was that Hubbert's theoretical requirements were carefully provided for.

Since 1939 several other experiments have been carried out, always with the dimensional aspect uppermost in the worker's mind.

To conclude this section, mention may now be made of the experiments conducted by the writer at Harvard in 1939. Dr. Griggs very kindly placed his machine-model at my disposal for some time and a scale model was built by me, using paraffin of varying melting points and wet potter's clay. By providing for rise of temperature in the experiment I was able to produce weakness in the paraffin.

The model (which took a considerable time to construct) represented broadly the structural conditions in the late Palæozoic tract between Newcastle and Tamworth, about Upper Marine or early Upper Coal Measure time (i.e. late Permian). The model embodied the gently folded strata existing at that stage of the late Palæozoic disatrophism, as well as the area of geosynclinal development south and west of the Hunter District. The orientation of the model was arranged so that when placed upon the waterglass substratum of the machine a subcrustal drag could be imparted to one side (the north-eastern side of the area), thus representing the operation of the Hunter-Mooki Thrust System with the south-westerly directed movement of the overthrust block. This was achieved by using one rotating drum. Several experiments were carried out and the total result was very instructive, tending to confirm the thesis that the unique character of the Thrust System is due to fracturing taking place after some earlier folding, the uprise of the thrust sheet being accomplished by adjustment with the folded structures in the truncated terrain (see Osborne, 1939).

Activities of the Tectonophysics Section of the American Geophysical Union.

The recently established section of Tectonophysics has been formed for the purpose of coordinating special researches upon tectonic matters where physical experiment and physical theory are applied. This section has an active committee under Professor Bucher, and with considerable funds, is endeavouring to clarify a good deal of confused data from geophysics concerning tectonics.

One project (see Bucher, 1942) that appeals to the imagination is designed to use the shelf-ice of the Ross Barrier, Antarctica, as a great natural apparatus for noting structural behaviour, such as bulging and fracturing of this great extended sheet. Such movements and ruptures are due to the interaction of land-ice and moving shelf-ice. Data obtained by Gould (1935, 1940) including excellent oblique air-photographs, are being assembled and studied with a view to recording possible ice-sheet tectonics which may help to explain extensive rock-tectonics that have marked the mobile thrust sheets of geological history.

Non-Diastrophic Structures.

Some very significant work in the last decade focusses our attention upon the rôle played by slump or gravity-collapse structures in sedimentary accumulations, and during their immediately subsequent history. The importance of such structures in oil-field geology has for a long time been appreciated by certain schools of workers.

In the Silurian of Wales, relatively large-scale structures have a regional development, and the full investigation of these has opened up wide avenues of discussion (see Jones, 1937, 1939).

Baldry (1938) has described interesting examples from Peru, and C. B. Brown (1938) has dealt with the theoretical aspects of gravitational sliding, especially with reference to the Tertiary sediments of Ecuador.

A most provocative paper by Carruthers (1939) dealing with contemporaneously contorted glacial sediments, puts forward an hypothesis based on englacial melting as the origin of such structures. This paper was eventually discussed in full (see *Q.J.G.S.*, 1940) and received a considerable amount of both support and adverse criticism.

A very thorough monograph on the origin, classification and significance of these contemporaneous structures is that of R. W. Fairbridge (D.Sc. Thesis, 1942, unpublished).

Petrofabric Analysis or Structural Petrology.

This difficult field of geology lies on the borders of tectonics and petrology, but is really more closely related to the former since fabric studies have been most frequently applied to the elucidation of tectonic evolution, thus being used as an aid to unravel deformations that have affected solid rocks. Less frequently, but with success, such analysis has been applied to investigation of purely igneous phenomena, such as flowage, and to grain orientation (depositional fabric) in sedimentary rocks.

After the establishment of this branch of geology at the hands of Sander (1930) and Schmidt (1932) pioneers introduced the subject to America, England and New Zealand. The main workers in these early studies were H. W. Fairbairn, Eleanora Knopf, F. C. Phillips, E. Ingerson and F. J. Turner. The appearance in 1938 of the memoir "Structural Petrology" by Mrs. Knopf and Dr. Ingerson placed the subject on a sound footing for English-speaking students.

The growth of interest in the structural behaviour of igneous rocks and the spread of the genetic attitude of mind towards structural geology were factors in the demand for improved microscopical analysis of flow-fabrics in igneous rocks, and for more intensive studies of the mechanism of plastic flow in deformed rocks. Thus in recent years the literature in this field has been slowly expanding and the scope of investigations has been widened (see Haff, 1938; Rowland, 1939; Fellows, 1943, etc.) and modifications of earlier general theory have been made.

A very important memoir by Fairbairn (1942) gives what amounts to an extension and partial restatement of his earlier valuable treatises (1935, 1937).

F. J. Turner has followed up his pioneering work by distinguished papers, especially that upon the schists of eastern Otago (1940), and the contributions of E. Cloos and Anna Hietanen (1941) are outstanding.

Analysis of growth-fabric in igneous rocks forms a species of research which is of a "liaison" character between field study of the tectonics of such rocks and the eventual determination of the full story of their petrogenesis and emplacement. A recent example of the importance of such interrelations is indicated by the details of Sir Edward Bailey's paper (1944) on the structure of

the igneous rocks of Rhum, and the future research-field in structural petrology thus indicated.

Whilst the value of fabric analysis in the elucidation of structural evolution and metamorphic condition in old terrains is unquestioned, it is to be stressed that a very discerning attitude must be exercised in such studies, as only the last deformative act is likely to be clearly displayed in the fabric-patterns that are obtained.

It may be argued that petrofabric studies are tedious and time-consuming, and that the possession of a knowledge of the technique (only obtained after much experience) may be regarded as a " luxury " item in the equipment of a petrologist or structural geologist, but the applications of petrofabrics to many economic problems as well as its proved value in general academic problems suggest that it will gradually have an increasingly wide circle of devotees.

It is surely significant that, with the exception of the Geikie textbook, all recent textbooks on structural geology give one or more chapters on petrofabric analysis, and in the important compilation upon ore deposits and structural features (1942), H. W. Fairbairn has contributed a chapter on fabric studies as applied to ore deposits.

Some Trends in Sedimentary Petrology.

It is particularly interesting to read the various historical surveys extant dealing with the development of sedimentary petrology which, since the period of the first world war, has been so rapid and broad in scope. Noteworthy in these advances have been the respective complementary phases of research. Thus (*a*) work in the descriptive or petrographic field, and (*b*) studies in sedimentation, have gradually unveiled a great province of geological activity and thought, wherein painstaking field work, accurate experimental techniques and philosophical discussion have erected an edifice of facts and principles as imposing as any set up by modern research in various branches of geological science.

The historical accounts of sedimentary petrology given in various textbooks and journals (see, e.g., Milner, 1940 ; Krumbein and Pettijohn, 1938) all indicate the rapidity of development during the last 25 years, and emphasise certain main factors contributing to these advances. Thus demands during the Great War in British industry for sands and other sedimentary materials led to intensive application of the methods of sedimentary petrology to the specification of industrial rock materials, compact or incoherent. With this phase of the growth of science the name of P. G. H. Boswell will be inseparably associated. Another factor in the remarkable growth of sedimentary studies was the influence and demands of the petroleum industry. Under its stimulus great interests in sedimentation have been generated and maintained.

The unfolding of research problems has widened the scope of this branch of geology and the great accumulation of knowledge has led to the appearance of several important books in the last decade. (See References.) Further, the continued success of the *Journal of Sedimentary Petrology*, established in 1932, has helped to coordinate researches conducted in widely separated centres.

While having noted the influence of the petroleum industry in promoting the studies of sediments, we may now indicate how methods of sedimentary petrology have in recent years been applied to other sciences. (*a*) We note first that in the developments in soil science during the last decade there has, in some quarters, been a swing back from support of the Glinka school to a recognition of the appropriateness of concentrating upon the geological approach to pedology. Thus soil mineralogy has developed steadily, as is shown by the increasing number of papers in pedological journals (especially the *Journal of the American Society of Soil Science*), in which sedimentary petrology techniques are solely employed for the solution of certain problems. It has been found

possible to correlate soils upon the data from heavy or resistant mineral suites; further, various geochemical studies of soils, especially in relation to animal ecology, have embraced the techniques of sedimentary petrography.

The recognition of the important rôles played by the clay-fraction of soils in base-exchange and in textural evolution and behaviour has led to acceleration of studies upon clay-minerals. X-ray analysis has now placed upon a firm foundation the mineralogy of the three great groups of clay-minerals, namely (*a*) the kaolinite group, (*b*) the montmorillonite group, (*c*) the hydrous-mica or illite group, and members of these series are vital constituents of sediments, so that advances in analytical study of the latter have been of assistance to pedology.

(*b*) The outstanding developments in recent years of the ceramic industry have called for more refined techniques in the separation and investigation of clay minerals and other ingredients of raw materials. The information available from sedimentary studies has been invaluable in such researches.

(*c*) In the growing researches upon the practical application of soil mechanics in engineering a considerable amount of field and laboratory procedure is along the lines of sedimentary studies. It is important for the engineer to know the sedimentary attributes of the various materials he is employing in constructional work. Studies of particle shape, mineralogy (especially in relation to clay-content, and geological context) are all important.

The great emphasis in recent studies upon the environment of sedimentation has inevitably led to the application of statistical methods for determining the environmental indices. In America, and elsewhere, the statistical approach to sedimentary petrology has been employed with much success, but it is clear that many of the present trends in this phase of the subject will have to be carefully assessed before standard procedures are stabilised. It was natural that statistical methods should so greatly develop when the various physical properties of sedimentary particles had to be determined and their frequencies interpreted. Such attributes comprise shape, size, roundness, density, orientation, etc. Application of statistical methods has in recent years led to the construction of many graphical aids depicting frequency and other relationships. Such aids are histograms, grainsize-maps, etc., and these are becoming more and more widely used in deductive work.

The implicatory importance of the resistant mineral suites of sediments in matters of (i) provenance, and (ii) petroleum sedimentology was affirmed by scores of workers during the period between the two world wars, and the criteria of mineral assemblages were considered valid in the elucidation of many problems, academic or commercial. It was customary to rely strongly on the data of lateral variation in interpreting provenance.

The state of tacit assumption that thus developed in regard to these principles has in recent years been disturbed by some splendid researches that have formed a dominant trend in the latest phases of modern sedimentology. The work referred to deals with the relative stability of minerals during transport to the site of deposition, and their stability during the post-depositional period.

The outstanding contributions of Edelman and Doeglas (1941), Russell (1939) and Smithson (1939-1942) and the careful appraisal of these researches by Boswell (1941) are among some of the most scholarly and scientific of contributions to modern sedimentology.

Dr. Smithson has revealed by very detailed mineralogical, statistical and cartographic studies the interrelations of the tectonic environment and the resulting stability of minerals. If a sediment is deeply buried during accumulation, the amount of post-depositional solution will be greater than that found in strata of higher levels in the column. Associated authigenic minerals and the

additions of outgrowths on some minerals (particularly zircon) are further expressions of the palæogeographical and tectonic controls.

Thus in the great field of sedimentary petrology we have in the last six or seven years witnessed some pronounced trends that can be enumerated summarily as follows:

(i) The study of post-depositional stability of minerals has revolutionised concepts of provenance as dependent upon data from lateral and stratigraphic variation in sediments.

(ii) Statistical and cartographic methods have developed enormously and have greatly helped the interpretation of genetic aspects of sedimentation.

(iii) Sedimentary petrology has contributed much to the field of soil mineralogy.

(iv) The demands from sister sciences regarding the exact nature of the clay minerals have required the application of the most refined separation methods based on sedimentary petrographic practice.

Some Trends in Economic Mineralogy.

A brief statement may now be made emphasising some developments in researches (essentially mineralogical) upon economic resources. (It is to be noted that the present remarks are not a review of advances in general studies of ore deposition.) The insistent demand in the last decade for fuller investigation, better production and conservation of mineral resources has led to some excellent researches. The specialised techniques of geophysical exploration have been greatly improved and much greater coordination of observations and results of geophysical surveys has been effected.

In the study of parageneses amongst the economic minerals, especially those occurring in a pegmatite environment, much careful research has led to the establishment of further criteria of association among the rarer elements and the more common minerals, which may be taken as "indicators" of the presence of minor constituents. The importance of some of these minor elements in various industrial processes, especially in the steel industry, has led to much refined spectrographic and X-ray investigation of minerals. Arising out of such work have come data concerning the control of rare-element associations in common or relatively common minerals. We are reminded at this stage of our discussion of the excellent account of the distribution and partition of the elements in the earth's crust given by J. S. Anderson in the first Liversidge Lecture of 1942 (p. 329). Details of recent work (e.g. Quirke and Kremers, 1943) concerning association of elements, confirm that order of crystallisation affinities, and temperatures of ore-formation, are intimately related to parageneses of minerals in various metallic groups.

Several experimental phase-rule studies with poly-component systems of metallic ores have been conducted and have thrown much light on mineral associations.

The use of the fluorescent lamp in prospecting for, and identification of minerals, especially the ores of tungsten and molybdenum, is now common practice, but the development of this technique has been greatly accelerated in the last five years.

Mineragraphic techniques have been consistently improved in recent years, and it is significant that of approximately 130 papers upon metallic ores examined by the writer only nine did not record the examination of polished sections.

The great underlying conceptions of crystal structure have, by their evolution since 1912, been fundamental to all mineralogical research, and this is

reflected in numerous recent papers and in the treatment of the subject matter in Volume I of the seventh edition of Dana's " System of Mineralogy " (Palache, Berman and Frondel, 1944). The influence of crystal-chemistry in mineralogical research (which became more easily applied after the appearance of Bragg's " Atomic Structure of Minerals ") has been further accelerated since the appearance of two excellent books (Stillwell, 1938, and Evans, 1939).

The growing industrial use of the common rock-minerals has given rise to much overhauling of information concerning the industrial properties and quantities of the minerals in question. A most important example of a specialised demand for a well-known rock-mineral is that of untwinned piezo-electric quartz, so vital in connection with radio transmission. The search for and evaluation of this special material has involved the carrying out of considerable refined physical and crystallographical research.

Another instance of refined mineralogical research upon a mineral mostly regarded hitherto as non-economic is seen in the investigation of the optical and isomorphous properties of the olivines in connection with the use of the magnesia-rich varieties for making certain refractory bricks.

Summarily, we may stress that some of the chief trends in research in economic mineralogy (apart from field studies) have been in the direction of the determination of

(i) more intimate details of mineral parageneses and geochemical relationships.

(ii) more accurate information concerning the composition of economic minerals, especially those that exhibit pronounced isomorphism ;

(iii) more crystallographic data (structural and morphological) of minerals, and the relation of such data to all known optical and chemical behaviour of minerals.

The War and Geological Science.

The effects of this war on modern civilisation and the resulting social revolutions that are in progress or will eventually develop are themes so profound that only one with a spirit and mind of Churchillian stature dare discuss them with any expectation of commanding attention.

However, as scientists we have all at various times throughout the conflict meditated over the effects of war upon science generally, and particularly upon the subject of our especial interest. Platitudinous statements about the misuse of science for war purposes have so often been made that repetition is somewhat unnecessary, but some reflections upon the relation of war and one's own subject is not inappropriate on occasions such as this. We may note two *main* categories of the application of geological science to war purposes :

(i) In the mineral industry and in respect of natural fuels.

(ii) In all other aspects, especially regarding problems concerning water supply, engineering materials, terrain and strategy.

I shall deal with the latter section first, and return to the subject of war and the mineral industry.

When the present war broke out, some senior geologists recalled the conditions of the last war in regard to the use of geology in war operations. In several parts of the British Empire (and no doubt elsewhere) articles appeared in technical journals, and in the Press, concerning this matter, and many discussions took place both in public and in private. Various reports and memorials were sent by academic and official geologists to governmental centres and to military headquarters. Having in mind the important contribution made on the Western Front and elsewhere by the numerically inadequate

geological staffs of the last war (activities in which the late Sir Edgeworth David played such a distinguished part), experts were agreed that adequate geological staffs should be attached to the chief military establishments. Apposite arguments were marshalled to support these contentions and details were given regarding contribution that could be made by geology to military activities, especially in the field of engineering geology, water supply, interpretation of terrain from air photos and general tactical considerations of invasions, especially along coastlines.

The reaction of governments and military authorities to such representations was disappointing, and except for the employment of a limited number of geologists for special and secret purposes the British carried on mostly by the adaptation of the services of geological surveys, especially in colonial areas. Very little was done in the Dominions, although some economic geologists displaced from their positions by enemy action were absorbed in geological surveys, or, in the case of Australia, were in some cases employed by the American army. The position in Australia has been that the army had very little in the way of appointments to geological staff personnel, although several men eventually migrated into geological work of importance after having entered the services by other avenues. We know that conditions have been vastly different in Russia and in the enemy countries, especially Germany, where considerable staffs of geologists were attached to military establishments. Of course, it has often been said that this war has not been one of " position ", as was the last, and that less need for geological staff would arise, but there are fallacies in this view.

(In parentheses, I can remind you that considerable bodies of advice have been given to defence authorities by university, governmental and other geologists in the course of their routine activities.)

The position outlined above has obtained not only in Australia, but is reflected in several important addresses and articles appearing in England at various times up to late 1942. Thus, in March, 1941, more than a year after England declared war, Prof. Boswell, in his presidential address to the Geological Society of London (1941), drew attention to the following :

(i) The lack of public and governmental interest in the subject of geology.
(ii) The small opportunities (apart from regular services connected with the mineral industry) for geologists to assist in the national effort.

He referred to several cases of deplorable waste of public money because of the absence of geological advice regarding various war constructional programmes dealing with camp and aerodrome sites, trenches, air-rair shelters, etc. In one case of the site for a proposed aerodrome and associated buildings the loss was more than £250,000 as a result of complete abandonment of the area due to impossible drainage conditions.

Boswell, speaking of general geology, ascribed the prevailing conditions as being largely due to ignorance of the part that geology can play in industry and in the changing orders of society. His remedy was that geologists must be their own propagandists and see that the community (and thus eventually its representatives in parliament) have more enlightenment.

Professor Boswell's address was later discussed by the Geological Society of London, and although several leading workers took a less pessimistic view of the situation, still the apathy of the authorities regarding the place of general geology in the war effort was regarded with much concern.

Coming to America, we next note a somewhat similar failure of the Government (although not so pronounced as in England) to see the importance of non-mineralogical geology in the war effort. America came into the war in

late 1941, and in late 1942 two articles appeared indicating this failure to appoint geologists to forward areas and on the home front.

Further, late in 1943 the National Research Council was circularising geologists regarding the setting-up of a committee on geological personnel relative to war work. This procedure arose out of needs consequent upon the final decisions in America regarding " occupational deferment " in critical professions.

So different is the picture from Russia. Although we do not know a great deal about the present scientific organisation of Russia, we have some knowledge which calls forth admiration and pardonable envy.

In connection with geology and Soviet economy, we have the reliable information that while in 1917 less than 1% of the Union had been geologically mapped, by 1931 Stalin regarded Russia as almost self-sufficient in mineral and other natural resources. And by 1931, realising the importance of geological surveys in a planned industrial economy, Russia was training hundreds of young geologists and had sent out several expeditions to the Urals, to the Kola Peninsula and elsewhere to determine places of prior interest in regard to mineral potentialities.

For the proper development of a great social and economic experiment in civilisation the authorities realised that nothing short of a great coordination of scientific work would provide Russia with the means of attaining the industrial potential to proceed to a dominant international place. Minerals (the raw material of much vital modern industry) had to be discovered and developed, and from such raw materials technology had to produce metals and other required substances. Thus geologists in great numbers and many metallurgists and geochemists were needed. In a fairly recent authentic article (on which I have based some of my remarks) we are told that by 1929 " thousands of geologists were at work and the geological sciences had acquired high national importance and recognition both in the government and among the mass of the people ". (Henry, 1942.) The eventual outcome in Russia was the establishment of the Central Geological Institute, which corresponds to the Geological Surveys of the British Empire and of America. In Russia this Institute employs a permanent technical staff of 600. Geologists and mineralogists in universities and research institutes number many score, and it is not too much to say that but for the bold plan of discovering, mapping and developing her vast resources Russia would not have been able to rise to the prominent place she has taken in this war, and that means our fortunes in the war would have been very different from what they are today. The article referred to above concludes : " Millions of school-children study geology in the field and in science laboratories. The man in the street reads of the progress of geological theory and discovery in his daily paper and leading geologists are public figures " ! !

Surely it is pertinent to draw attention to these facts about geology in Russia when we reflect on the rapid rise of the Soviet Union to its present state.

Turning now from the question of the status of geological surveys in Russia, I wish, very briefly, to consider the position in the British Empire and to contrast it with the conditions obtaining in America, our other great ally.

It is significant that, in November, 1943, the Institute of Mining and Metallurgy and the Geological Society of London held a great discussion on the " Contributions of Geological Surveys to Colonial Development and the Future of Geological Surveys " (1943). This symposium was considered relevant in view of the need for post-war planning and the economic development of the colonies (I am not referring to the Dominions).

The main trend of the long discussion can be summarised in the simple statement that in every colony there is to be read the same story of total inadequacy of funds, insufficient staff, even though the colonial geologists had

to deal with vital problems of water-supply in difficult areas. The heartbreaking conditions that many pioneering colonial geologists had to endure in the past have not been supplanted by improved conditions simply because the Colonial Officers and the British Government do not realise the functions and importance of geological surveys in the development of their territories. The conference passed certain resolutions and promised action which need not be discussed here.

When we come to America we find considerable public recognition of the importance of geology in the national economy. Geological surveys exist in all States and there is a large Federal survey. Apart from these bodies there are Bureaux of Mines, Water Supply Commissions and many other organisations employing geologists and mineralogists, thus closely identifying geological work with general public services. The record, present organisation and geological programmes of the United States Geological Survey call forth great admiration, and it is obvious that the rise of America to pre-eminence as a nation in recent generations is due in no small measure to the development of her great mineral wealth, potentialities that can only be satisfactorily brought to light by geological services.

This brings us to Australia. Here there must be mixed feelings concerning this subject. The State Geological Surveys, without exception, are all understaffed and have known greater days in the past. This means the staffs are heroically carrying on the essential duties of their important offices. In the Federal sphere the situation is brighter. Following the pioneering work of Dr. Woolnough in his geological advisory activities, Dr. Raggatt has now organised the Mineral Resources Survey on a sound footing, and its rapid development and businesslike attack upon the vital problems presented by the demands of war industry for minerals and fuels constitute a heartening chapter in the history of official geological activities in Australia. But the future development of the Mineral Resources Survey is a very important matter. Australia must, in the post-war era, have definite national policies regarding minerals and fuels. Further, in order to be a full participant in international affairs and to rise to the full status required for a great base country in the evolution of world security, and especially equilibrium in the Pacific region, this country will need a fully organised, adequately staffed, national geological survey. We have seen the importance of such organisations in the industrial rise of America and Russia, and we take note of these examples.

Therefore I was glad to report earlier in this address that we had, as a Council, given support to the move made by the Australasian Institute of Mining and Metallurgy in requesting the Commonwealth Government to set up a full Federal Geological Survey. Apart from being a key public service, such a survey would greatly help in the evolutionary change from war industry to peacetime activities.

The lines of my address just traced lead us into the great question of the rôle of minerals in international affairs, both in times of peace and of war. This is a wide field of discussion, but the significant points agreed upon by most authorities are these :

(i) The growth of mineral industries has transformed nations from being largely agricultural to becoming highly industrialised.

(ii) Countries well endowed by nature with mineral and fuel raw materials are those likely to occupy foremost positions in international affairs.

(iii) The inequitable distribution of mineral resources in the world favours Russia, Britain and America and has always placed Germany, Italy and Japan in unfavourable (or "have-not") positions.

(iv) The last two great conflicts have arisen largely as a result of the ambition of aggressor and dictator nations to obtain a better distribution or bigger share of the world's mineral wealth, so as to be more secure in development of modern industry.

(v) By importation (with hoarding), bargaining, and later by annexation and the employment of " Hitler " tactics Germany was able to build a war industry and arm herself to such an extent as to be ready to take risks and challenge the democracies. Italy and Japan adopted similar policies, in lesser degree.

Thus we see that if war is to be prevented in the future some radical changes in regard to the great problems of distribution of raw materials will be necessary. The whole matter of the future economic equilibrium of the world is, of course, inextricably interwoven with the political aspect. In this broad field lie the important concepts of the social implications of science, the use or frustration of science, and the relations of science to political ideals. It may be said to be a problem of the relations between political equilibrium and economic equilibrium in the world. However, I have decided to avoid attempting to speak at length this evening on the social and political relationships of science, as it is a very involved subject.

What I want to say is that the great problems of world distribution of raw materials, and the rehabilitation of peoples in the devastated areas, both allied and enemy countries, must inevitably involve an international minerals' policy or some such principle.

Many leading geologists in America and elsewhere (see grouped references below) have written on this subject. America, as is characteristic of her, has at different times since 1938 enacted legislation leading with " critical " and " strategic " minerals and concerning national mineral policies generally. Further, some government committees have prepared alternative schemes for the preservation of peace, by considering minerals in the peace settlement. One result of these trends of thought is that seven important books have been written since 1940 setting forth the rôle of minerals in human affairs.

In regard to post-war schemes there are many alternatives, but some of the main suggestions as set out by C. K. Leith (1940) are :

(i) Maintenance of the present conditions, i.e. unequal distribution and retention of control by the great Allied countries.

(ii) Changes in the *status quo*

- (*a*) by reviewing the present cartel system of distribution and setting up a Cartel Commission in which government and public bodies have more influence.
- (*b*) by modification of details of tariffs and quotas ;
- (*c*) by redistribution of colonial possessions.

(iii) By operations of mineral sanctions, if need arose.

Concerning this urgent problem a symposium, held last year by the American Institute of Mining and Metallurgical Engineers, produced views which mostly leaned towards the establishment of better distribution, but with an over-all control by power in the form of some international armed police force. Even Dr. Leith, who has been the outstanding figure in America in connection with this subject, and who has endeavoured to find the least violent way out of the problem, has reluctantly come to the conclusion that " something more than sweet reason is necessary ". What does seem vital, if the Atlantic Charter is to be sustained in post-war councils, is the establishment of an International Minerals and Fuels Commission, working in conjunction with such bodies as U.N.R.R.A. and any world council that may develop from U.N.C.I.O. ; such would directly control

movements of mineral and natural fuel resources, thus indirectly limiting the industrial capacity of nations that appear to be capable of repeatedly disturbing world equilibrium.

However, since wars are deeply rooted in human nature, I would point out that any agreement purely on a technical and materialistic basis will fail and we will be faced with a third world catastrophe. Certainly means of enforcing peace will be needed for a long time, and some kind of armed force may have to be set up, but ultimately the solution must lie in international goodwill and understanding. As Sir Henry Dale said to members of the Royal Society of London recently (1943), " we cannot put aside the responsibility for the future of mankind ", and in Churchill's words, " the scientists of the world must be united by a common bond of a single purpose that overrides all bounds of race and language " (1943). The ideal must be higher than on the plane of purely material well-being. The great controlling powers must view themselves as trustees of world peace and the stability of civilisation, and so develop international committees as to ensure that machinery is set up to prevent further wars.

Some Effects of the War Upon the Progress of Geological Science.

One general effect of the war upon science has been that great numbers of research workers in many countries have been taken from pure research and switched to various industrial and technological activities dominated by war demands. True it is that in many branches of scientific endeavour, applied to war purposes, there have been epochal discoveries that will modify and even revolutionise continuing researches in certain fields in the future. But viewing the matter in its broadest phases, it is clear that the war will have adversely affected a great number of young research workers whose scientific careers had not progressed very far, but had shown great promise. During the greater part of a decade in the lives of such workers there will have been an absence of that detachment from material or industrial applications of scientific results which is so vital to disinterested research. The ideal of pursuing science for its own sake, the absence of regimentation of scientific workers, and the exercise of intellectual freedom have, in the war years, been supplanted by a war-dictated planning of research activities designed largely to bring about the destruction of the enemy's industrial power and military man-power. The effects of such conditions will surely be felt in the decade that follows the war and serious damage to the spirit of pure scientific research has undoubtedly been done.

However, it is probable that the scientific world will recover more quickly than it did after the last war, and the advances in such fields as aircraft development, drug research, medical and dental techniques and in a host of other fields will be reflected in a much more enlightened mode of civilisation, if only peace can be maintained.

Coming now to particular aspects, it is clear that pure geological research (i.e. those studies that can be regarded as in no way specifically directed to practical application) has not been affected much by the war, except very indirectly by the interrelations of all fields of geological knowledge. But the amount and degree of the work done certainly have been much less than if war had not come.

Thus some of the trends recorded above persisted through the war period, but with less research momentum than would be expected under conditions of peace.

In branches of geological science more definitely related to practical aspects of modern civilisation there have been very noticeable effects. Most important has been the far-reaching influence of war on the mineral industry. These two are vitally linked, and H. G. Raggatt, in his Clarke Memorial Lecture of

1943, gave an excellent and significant account of the relations of the present war and the Australian mineral industry.

The leading effects of the war upon academic and economic mineralogy have been in the direction of prompting the marshalling of all agencies for the study of mineral-formation and ore-occurrence, as well as inspiring the invention of specialised techniques in mineral prospecting and calling for the most refined metallurgical practice. Stocktaking activities, both in the field and in the offices of government departments have been most extensive and thorough, leading to a wide and up-to-date literature concerning the mineral resources of many countries. This literature embraces many books, statistical compilations, reports and bulletins dealing with reserves of strategic minerals.

In the great impetus upon the development of economic mineralogy the contribution of structural geology has been marked, particularly in connection with the control of mineralisation, and thus I link together the previously discussed trends in foundational physical geology and in structural geology with the more specific scientific work consequent upon an expanding mineral industry. My contention is that the demand for greater mineral production has indirectly been a factor in the acceleration marking the trends of non-mineralogical research detailed above.

Connecting the war and developments in the sphere of sedimentary petrology I see a link expressed in some of the great advances in soil science, and behind that in agriculture itself. The war has thrown into relief the vital need for rationalisation and planning in agriculture because food production and distribution is going to be one of the greatest tasks in the coming years. After all, the crust of the earth contains all the minerals and natural fuels needed by man and the decomposition of the outer crustal surface provides him with soil, vital to his existence. Modern pedology, especially in its application to agriculture, is calling more and more for assistance from mineralogy, geochemistry and particularly for the application of the principles and techniques that have been established in sedimentary petrography. Thus I link up some of the trends in this branch which we have already considered with a definite effect of the war upon agricultural development.

Spectacular, and of vital strategical importance, has been the contribution to the war of the interpretation of aerial photographs by geological and geographical experts attached to intelligence sections of the Services, particularly of the Air Force. In no theatre of war has this type of tactical research been more brilliantly conceived and more successfully applied than in the Pacific. The detailed study from the air of shore-lines, particularly those strands bound by coral reefs, and geological observations on the ground have contributed in a most vital way to the successful amphibious operations connected with the attacks upon Japanese island strongholds. The war has been responsible for a rapid advance in all aspects, theoretical and practical, connected with the use of this great weapon for the solution of geological problems.

The Outlook on Some of the Frontiers of Geological Science.

Geology has been expanding in many branches. I have had time to suggest only some advances in three or four fields, but there is a fascinating story to tell of the advances in other branches, such as petrology and palæontology, particularly the growing trends in the application of micropalæontology to oil geology.

Standing on the frontiers of geological science, one may get some visions of possible developments. Dealing only with those aspects considered in the

address, I venture to suggest that in the more prosperous countries we shall probably see the following expansions :

(1) In the border region of geology and geophysics, a great increase in the application of experimental studies to fundamental physical geology, and the steady development of the investigation of the structure and constitution of the sea-floor.

(2) In structural geology :

(*a*) A greater concentration upon "genetic" field studies, with application of dynamic principles, and a great development in gravity and seismic surveys on land and sea to determine the structural features.

(*b*) In megatectonics the study of orogenetic evolution will be guided largely by the concepts of the convection current hypothesis of diastrophism.

(*c*) Studies of fracture-patterns and fold trends of regional extent will be based on the assumption of underlying controls envisaged in the statement under (*b*).

(*d*) The production of tectonic maps, local or regional, will become more common.

(*e*) The structural behaviour of igneous rocks will occupy more attention. The recognition of ring structures, less complicated than those of the British Tertiary, will follow a close dynamic analysis of the field data from many intrusive areas.

(*f*) A slow but gradual increase in petrofabric analyses, with more emphasis upon igneous structures than has been made in the past.

(3) In general economic mineralogy an increased interest in genetic aspect of the structural control in ore deposition. More attention will be paid to the signification of various boxworks.

A greater application of geochemistry and refined physical techniques to mineral assemblages generally, and to the mineralogy of pegmatites in particular. An expansion of geophysical attack on the problem of ore-finding.

(4) In sedimentary petrography further development of statistical methods ; increasing attention to the stability of minerals in sediments, and interest in the behaviour of clay minerals in soil mechanics.

In general sedimentology an intensive study of sea-floor deposits and other modern sediments in an endeavour to interpret the environmental conditions of more ancient sediments.

Also a trend towards experiments with compaction and induration of sedimentary materials.

Any contemplation of these possible developments and the equally important trends in other geological branches brings home to members of our science an appreciation of the ever-widening sphere of research, within which it is our privilege to work. All basic science can be regarded as contributive to the onward march of civilisation, and therein lies the great responsibility of geologists along with their fellow scientists in building a world order of human welfare wherein mankind can naturally and constructively use the resources of nature so that they become the munitions of Peace.

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GENERAL GEOLOGY OF THE WELLINGTON DISTRICT, N.S.W.

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and Margaret J. Colditz, B.Sc.

With Plates I-III.

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Introduction.

The town of Wellington is situated on the Main Western Railway between Orange and Dubbo, 255 miles by rail from Sydney. It lies on the Central-Western Slopes at an altitude of 1,000 feet and is at the junction of the westward-flowing Bell and Macquarie Rivers.

The area discussed in this paper covers about 500 square miles, its northern boundary being the south-eastern limit of the intake beds of the Great Artesian Basin. It includes portions of the Counties of Bligh, Gordon, Lincoln and Wellington and covers in all about twenty parishes.

The boundary of the Jurassic rocks and the geology of parts of the parishes of Galwadgere, Mumbil (centre) and Wellington (south-west) were mapped by the Geological Survey of New South Wales. This work, with some modifications, has been used in the compilation of the geological map of the Wellington district.

A generalised geological map of the district in the vicinity of Wellington was published by A. J. Matheson in 1931, but this has been considerably altered.

The first geological report on the district was made in 1839 by Major T. L. Mitchell, who published a map of the Bell River valley from the Caves to Wellington showing red sandstone, alluvium, gravels, limestone and trap rock (andesite). He described the caves in detail, giving plans and sections as well as a list of fossils found therein.

The Wellington Caves created a great deal of interest in scientific circles in the middle nineteenth century and were described in a parliamentary report entitled "Exploration of the Caves and Rivers of New South Wales" (1882).

More recent reports have been made by A. C. Lloyd (1931), L. J. Jones (1935), Dorothy Hill (1942), Elizabeth M. Basnett (1939, 1942) and Margaret J. Colditz (1942). The bibliography of the present paper has been made as comprehensive as possible.

We wish to thank the Government Geologist for permission to use unpublished maps; Dr. Dorothy Hill and Dr. Ida Brown for palæontological assistance; Dr. Germaine Joplin for her encouragement; Miss Marion Breckenridge for assistance in the preparation of the manuscript; and the people of the Wellington district for hospitality during field work.

The principal formations which have been examined are:

(1) Ordovician cherts.

(2) Silurian strata.

- (i) A Volcanic Series consisting of andesites and pyroclastic rocks.
- (ii) An Upper and a Lower Sedimentary Series of shales, tuffs and limestones.

(3) Lower and Middle Devonian limestones and shales.
(4) Upper Devonian shales, sandstones and conglomerates.
(5) Kamilaroi coal measures.
(6) Jurassic sandstones and grits.
(7) Tertiary flows and gravels.
(8) Pleistocene and Recent cave-deposits, sands and gravels.
(9) Intrusive rocks.
  (i) Sills of lamprophyre of Silurian age.
  (ii) A dolerite intrusion of epi-Silurian age at Wuuluman.
  (iii) Two granitic intrusions of (?) Kanimbla age named the Wuuluman and Yeoval granites.
  (iv) Dykes and small irregular intrusions of probable Tertiary age.

Ordovician.

Rocks of Ordovician age were first recorded by L. J. Jones (1935) from two localities, viz. a road quarry $1\frac{1}{2}$ miles north-west of Wellington on the Mudgee Road (Res. 6, Par. Nanima) and near Apsley Railway Station (Por. 281 and N.W. of Por. 109, Par. Wellington). At the first-named locality the outcrop is partly masked by soil, while at Apsley three small outcrops are separated by Silurian andesitic rocks. The most westerly of these is flanked on the north by limestone of probable Middle Devonian age (Fig. 1).

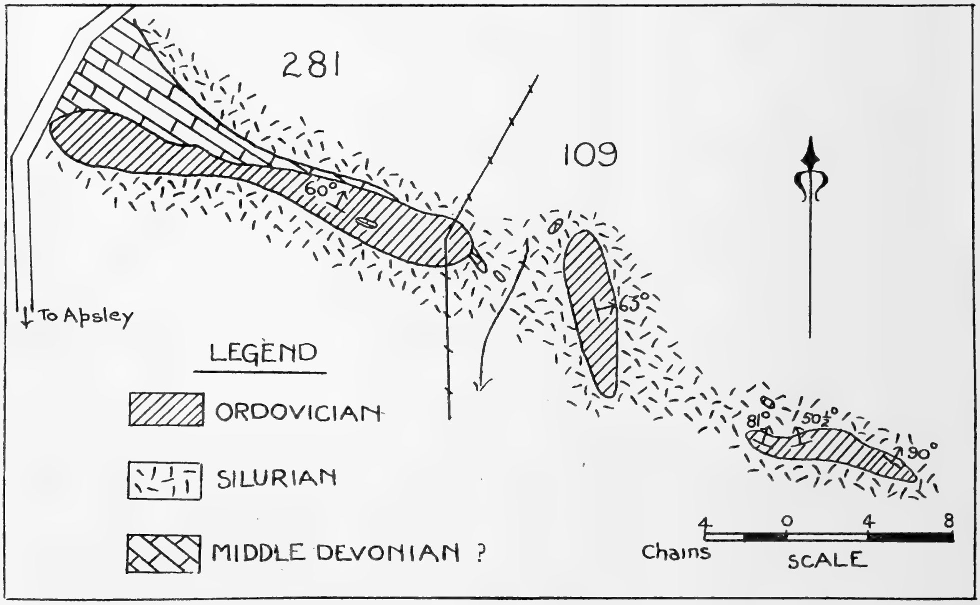


Fig. 1.

In both areas the rocks have been highly folded and puckered and show almost vertical dips (Pl. I, Fig. 1). They are hardened claystones and cherts with fine banding and vary in colour from light to dark grey. Minor faulting and brecciation are commonly developed.

The following graptolites have been identified by R. A. Keble and K. M. Sherrard (1938):

Res. 6, Par. Nanima.

Diplograptus (*Orthograptus*) *calcaratus* var. *vulgatus*.
D. (*O*). *calcaratus* var. *basilicus*.
D. (*O.*) *truncatus* cf. var. *socialis*.
D. (*O*). *truncatus* var. *intermedius*.
D. (*O.*) *rugosus* var. *apiculatus*.
? *Dicellograptus* sp.

Pors. 281, 109, Par. Wellington (Apsley).

Diplograptus (*Orthograptus*) cf. *truncatus*.
D. (*O.*) *truncatus* var. *intermedius*.
Climacograptus biconnis.
C. sp.
Dicranograptus sp.

It is considered by Keble and Sherrard that the beds are equivalent to the Middle Eastonian of the Upper Ordovician of Victoria, the Apsley beds being the older of the two occurrences.

Silurian.

The Silurian sequence has been divided into a Volcanic Series and an Upper and Lower Sedimentary Series in order to map the structure to the north-east of Wellington where this grouping of the rocks is well defined. West of the Catombal Range and south of Apsley the same grouping has been used in the maps and sections, although it has been necessary to include some volcanic rocks in the Sedimentary Series and some sediments in the Volcanic Series.

The Volcanic Series lies between the Upper and Lower Sedimentary Series and corresponds with the Igneous Stage suggested by Matheson (1930), while the Sedimentary Series include his Lower Shale, Lower Limestone and Upper Shale Stages, as well as part of the Upper Limestone Stage.

(i) *Volcanic Series.* This series consists of interbedded lavas and pyroclastic rocks with occasional small lenses of limestone. The lavas are usually aphanitic types with phenocrysts and are grey, green or purple in colour according to the type of deuteric alteration present. Andesitic xenoliths are fairly common in the lavas and are easily seen because of this variation in colour.

Felspar, augite and hornblende occur as phenocrysts which vary in size and relative abundance in different flows. The average length of the augite phenocrysts is from 1 to 2 mm., but in some cases they reach 1 cm. (N.E. corner of Por. 47, Par. Nanima.) A glomeroporphyritic arrangement of the smaller crystals is not uncommon. The amphibole phenocrysts are brown, brownish-green and yellowish-green in colour, and though usually small, the long slender prisms may reach 3 mm. and even 5 mm. in length. The felspar phenocrysts vary greatly in size, the largest being 5 or 6 mm. and the smallest being hardly distinguishable from the groundmass.

Most of these lavas are andesites, but there are also trachyandesites, basalts and trachybasalts. The exact lava types which have been determined are as follows: hornblende-andesite, augite-hornblende-andesite, hornblende-augite-andesite, pyroxene-andesite, andesitic basalt, porphyritic basalt, hornblende-trachyandesite, hornblende-pyroxene-trachyandesite and porphyritic trachybasalt.

The pyroclastic rocks consist of andesitic tuffs, breccias and agglomerates and occasional crystal tuffs. In all but the crystal tuffs multi-coloured fragments of andesite are bound together by a tuffaceous matrix which is usually of an

andesitic nature. Towards the top of the Volcanic Series large fragments are found in the breccias and sometimes pebbles of quartz-dolerite, slates and quartzites occur in these, associated with the andesites.

The coarser breccias and agglomerates are often difficult to distinguish from the xenolithic lavas. The latter contain rounded andesitic xenoliths up to several inches in diameter. Both rock types weather to large rounded boulders which are occasionally more than 6 ft. high and resemble granite tors. Where the outcrops have disintegrated there remains an assortment of andesitic pebbles which may have been derived from either a xenolithic lava or a breccia.

In general the crystal tuffs are fine, cherty rocks which show sub-conchoidal fracture, are medium to dark grey in colour, and in thin section appear to be strongly recrystallised. These rocks contain tiny crystals of albite-oligoclase and quartz embedded in a very fine-grained matrix of similar material. Unlike the andesitic types, these rocks contain no hornblende or pyroxene.

Rhyolites occur along the summit of the Wuuluman Hills where they overlie slates. They have been tentatively grouped with the Silurian strata.

(ii) *Upper and Lower Sedimentary Series.* The Lower Sedimentary Series occurs south-east of Apsley and consists of brownish shales and grey limestones. The outcrops range from argillaceous beds of limestone a few yards wide to massive grey bedded limestones several hundred yards in width. Narrow bands of andesite are interbedded with the sedimentary rocks.

The fauna includes *Pentamerus knightii* and *Tryplasma* sp. An outcrop in Morangulan Creek (Por. 134, Par. Wellington) contains *Halysites*, *Entelophyllum* and Spirifers.

The Upper Sedimentary Series is typically developed between Wellington and Wuuluman. In this area it consists mainly of shales, slates and limestones. The latter are usually of limited extent and of tuffaceous character, passing both horizontally and vertically into tuffs and slates. A great variety of tuffs is found in this series, amongst them being greenish-grey rhythmically-banded types and chocolate coloured tuffs. West of the Catombal Range there is a greater development of shale and tuff with very little limestone. A band of garnetiferous tuff extends from the Macquarie River southwards, and a little further to the east the same rock type crops out on the Yeoval Road, west of Curra Creek. It forms low ridges and weathers to granite-like tors and a coarse sandy soil. It is a reddish, coarse-grained rock with crystals of felspar and irregular masses of red garnet as much as one inch in diameter.

Fossils are not plentiful, but a fairly rich fauna occurs in limestone in Por. 10, Par. Nanima, viz.: *Tryplasma lonsdalei* Eth. fil., *T. lonsdalei* var. *scalariforme* Eth. fil., *Spongophyllum ? shearsbii* Chapman, *Halysites* sp. *Halysites* sp. has also been collected from Por. 5, Par. Tenandra and Por. 23, Par. Galwadgere.

The junction between Silurian and Lower and Middle Devonian is not clear owing to a lack of fossil evidence and to an abundance of soil and alluvium to the west of the Catombal Range. For this area the Silurian boundary has been tentatively placed above the compact slates and tuffs which occur to the north-east and west of the Catombal Range.

DEVONIAN.

Lower and Middle Devonian.

Limestones and shales of Lower and Middle Devonian age extend along the flanks of the Catombal Range and stretch from its northern limit to the Jurassic sandstones at Geurie.

The limestones are very massive and often show well-defined bedding. Strong outcrops occur continuously from near the Wellington Caves to the Parkes

Road on the western side of the Bell River. Occasional shaly beds occur here also, but they are more common in the northern and western outcrops. The shales are buff-coloured and friable.

The first Devonian fossil recorded from these limestones was *Rhizophyllum enorme*, which was discovered by E. M. Basnett in 1937 (Brown, 1937). Since then a considerable amount of collecting has been done by Dr. G. A. Joplin, Miss Alma Culey, Dr. Dorothy Hill and the authors of this paper. Accurate determinations have been made by Dr. Hill (1942). On the palæontological evidence thus obtained, the limestones have been grouped with those of Lower and Middle Devonian ages in eastern Australia. Those of Lower Devonian age may be equivalent to the Garra beds at Molong (Joplin and Culey, 1938). More palæontological work must be done, however, before a definite boundary can be drawn between the Lower and Middle Devonian limestones at Wellington and they have been grouped together in the map which accompanies this paper. Localities which have been identified as either Lower or Middle Devonian are included in Table I.

The Middle Devonian beds crop out at the northern limit of the Upper Devonian rocks and extend north-west almost to Geurie.

The Lower Devonian (Garra) beds fringe the Middle Devonian to the east, north and west and include the limestone of the Wellington Caves.

Although the limestone-shale facies is variable, the Lower Devonian beds consist for the most part of limestone with shaly bands and grade into shales in which an abundant brachiopod fauna with some trilobite remains is preserved (Por. 16, Par. Curra). The Middle Devonian beds are usually of a massive limestone with some shaly bands which may contain brachiopods.

The Wellington Caves limestone has previously been correlated with the Silurian limestone of Jenolan Caves. Dr. Hill (1942) suggests a Lower Devonian age from the examination of fossils from two localities in the neighbourhood of the Caves. The area is one of minor folding and faulting (Pl. I, Fig. 3) and further collecting to the south of the Caves may result in the discovery of Middle Devonian or of Silurian beds.

Upper Devonian.

The Upper Devonian rocks of the Catombal Range have been described in considerable detail by Matheson (1930). As the " Catombal Series " he describes those beds which contain *Lepidodendron australe* and overlie the *Spirifer disjunctus* horizon or " Transition Stage ". He suggests that the latter may be Lower or Middle Devonian, but as *Spirifer disjunctus* indicates an Upper Devonian age elsewhere, it is suggested here that the two Series be grouped in the Upper Devonian as the Catombal Series.

The rocks are red to purple in colour and consist of shales, sandstones and conglomerates. The latter is very coarse and contains pebbles up to 12 inches in diameter but is often banded with sandstone. It forms bold outcrops as it is more resistant to erosion than the surrounding rocks (Pl. I, Fig. 4).

Minor folding is absent, in contrast to the crumpling of the underlying limestones but the folds are steep. They are well shown in road cuttings along Curra and Bushranger's Creeks.

Kamilaroi.

The occurrences of Kamilaroi rocks have been recorded by the Mines Department in and near the district mapped. In 1890 one hundred tons of coal were removed from a flat-lying 3-ft. seam in a 60-ft. shaft in Por. 215 or 127, Par. Micketymulga. The deposit is covered by 27 feet of alluvium and consists of shales and thin coal seams.

TABLE I.

	Middle Devonian.										Lower Devonian.						
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII
Acanthophyllum æquiseptatum Hill	x	x					x										
A. cf. *mansfieldense* (Dun)																x	x
Acanthophyllum sp.						x											
"*Cystiphyllum*" *conjunctum* Hill													x				
"*Cystiphyllum*" sp.												x	x	x	x		
Disphyllum gemmiforme (Eth. fil.)				x													
D. mesa Hill													x	x			
Eddastræa expansa Hill									x								
Eridophyllum bartrumi Allan				x				x									
E. immersum Hill															x		
? Grypophyllum ? aggregatum Hill				x								x					
Phillipsastræa aperta Hill									x								
P. oculoides Hill				x													
P. speciosa Chapman	x	x															
P. sp. aff. *P. speciosa* and *P. linearis*									x								
Pseudamplexus princeps (Eth. fil.)		x			x							x	x	x			
Radiophyllum aff. *arborescens* Hill and Jones											x				x		
Rhizophyllum enorme Eth. fil.													x	x			
Tryplasma columnare Eth. fil.																x	
T. ? lonsdalei Eth. fil.													x				
T. wellingtonense Eth. fil.														x	x		x
Xystriphyllum dunstani (Eth. fil.)		x?		x		x?		x									
X. magnum Hill			x														
Favosites allani Jones									x								
F. basalticus Goldfuss var. *moonbiensis* Eth. fil.												x					
F. bryani Jones	x	x							x								
F. goldfussi d'Orbigny												x		x			
F. gothlandicus Lamarck														x			
F. sp.													x	x			
Heliolites daintreei Nich. and Eth.															x		
Pleurodictyum bifidum Jones					x							x					
Syringopora sp.												x	x				
Receptaculites ? australis														x			
Amphipora sp.										x							
Stromatoporoidea undet.									x				x				
Atrypa sp.									x			x		x			
Rhynchonellidæ		x							x								

Key to Table I.

I. Wellington-Dubbo Road, 12 miles from Wellington, Parish Geurie.
II. Por. 59, near Por. 39, Par. Geurie.
III. Por. 247, Par. Micketymulga (north of road).
IV. Por. 247, Par. Micketymulga.
V. Por. 206, Par. Micketymulga.
VI. Pors. 206/59, Par. Micketymulga.
VII. Por. 62, Par. Micketymulga.
VIII. Holmes Estate, Par. Micketymulga.
IX. Por. 50, Par. Curra.
X. Por. 94, Par. Wellington.
XI. Por. 42, Par. Woorooboomi.
XII. Por. 82, Par. Micketymulga.
XIII. Por. 30, Par. Gundy.
XIV. Pors. 170, 172, 166, Par. Curra (Fingerpost).
XV. Por. 172, Par. Wellington (Caves Reserve).
XVI. Por. 46, Par. Wellington (turn-off to Caves from Orange Road).
XVII. "Wellington"—probably Wellington Caves.

Other deposits occur to the north of Mumbil Trig. Station and at Burrandong where coal-measures crop out on both sides of the Macquarie River (Jones, 1936). They are chiefly sandstones and conglomerates which rest unconformably on Silurian rocks, and are correlated with the Upper Coal-Measures of New South Wales.

Jurassic.

The Jurassic beds consist of coarse yellow to reddish-brown sandstones and grits, with occasional bands of shale. The coarse, porous nature of the sandstone suggests that it belongs either to the Erskine Beds (Lloyd, 1934) or the Pilliga Beds (Dulhunty, 1939). They form low cliffs particularly to the north of the Ponto Bridge and have a gentle dip to the north-west overlying unconformably the Palæozoic rocks. These beds form the south-eastern limit of the intake beds of the Great Artesian Basin. An outlier of Jurassic sediments occurs at Mt. Bodangora, about 12 miles north-east of Wellington. The deposit is 25 feet thick, consists of ferruginous sandstone and grit, and is overlain by Tertiary basalt (Pl. I, Fig. 5).

Tertiary.

Rocks of probable Tertiary age are small, numerous and varied in character. They occur in the form of

(i) gravels,
(ii) flows which sometimes overlie gravels,
(iii) Intrusions (these are discussed in another section of this paper).

The field occurrences of flows and gravels have been described by Colditz (1942). Mention may be made of the fact that gold-bearing Tertiary gravels, as much as 60 feet in thickness, underlie the basalt along the Bell River near Newrea. In Por. 10, Par. Terrabella quartz gravels cemented with iron oxide form low hills to the east of the Little River.

The flows along the Bell River and those at Mt. Bodangora are basaltic varieties. In the last-named locality Jurassic grits are capped with an even-grained olivine basalt which contains titan-augite, iron ore, analcite and some zeolites. At the foot of the mountain, below the level of the grits, a small, conical hill is formed of porphyritic olivine basalt with a groundmass composed largely of augite and iron ore. This rock probably occupies a vent through which the overlying basalt was extruded.

Olivine-bearing trachybasalt crops out in Pors. 75 and 92, Par. Nanima, and in Por. 130, Par. Ponto. In Por. 75 the flow is overlain by a phonolite, while in Por. 130 the trachybasalt lies above a trachyte which shows good columnar jointing. Plagioclase phenocrysts are abundant in these rocks, but orthoclase is rare. The crystals are highly corroded and altered and in places are crowded with granules of iron ore and pyroxene. The fine-grained groundmass consists of plagioclase and some orthoclase with green and titaniferous augite and yellowish olivine.

Only two trachytes have been examined in this section. These both show flow structure, are fine-grained, and contain a green sodic variety of pyroxene. The rock from Por. 75, Par. Nanima contains analcite and small crystals of nepheline. Yellowish olivine is present in the one from Por. 130, Par. Ponto.

In Por. 13, Par. Geurie, there is a small outcrop of melilite basalt which is either Tertiary or Jurassic in age. It consists of olivine, ophitic titan-augite and small laths of melilite.

Pleistocene and Recent.

Deposits of post-Tertiary river gravels occur along the courses of the Bell and Macquarie Rivers on old river terraces (Colditz, 1942). The Wellington Caves are filled with thick deposits of red cave earth which contains multitudinous bones and teeth of Pleistocene mammalia. Some of the upper caverns are completely filled and surface-waters have cemented the topmost material. Below the surface, however, the earth is friable and the bones are easily separated from the matrix. In the early years of this century these deposits were used unsuccessfully for superphosphate and large quantities of valuable fossils were crushed for fertiliser.

A detailed list of references dealing with the palæontology of the fossils is given by C. Anderson (1933).

Intrusive Rocks.

The intrusive rocks of the district vary in age from Silurian to Tertiary, the oldest being the lamprophyres, which were intruded at the close of the Silurian period. The Wuuluman dolerite and associated keratophyre were injected some time after this but before the intrusion of the granite. The Wuuluman and Yeoval granites belong to a later period and are probably of Kanimbla age. Still later, probably in Tertiary time, alkaline dykes and plugs were injected.

(i) *Lamprophyres.* The lamprophyres occur as a group of north-south trending sills in the parishes of Wuuluman, Nanima and Bodangora and have been described in detail by E. M. Basnett (1942). Augite-lamprophyre, augite-plagioclase-lamprophyre and hornblende-lamprophyres occur, but of these only the augite-lamprophyre is widely distributed. The rocks are green to purple in colour and contain numerous phenocrysts of diopsidic augite which are usually replaced partly or entirely by amphibole as a result of metamorphism. Directional structures resulting from dynamic metamorphism are common and in the vicinity of Poggy Creek, where faulting occurs, the rocks are highly schistose.

(ii) *Wuuluman Dolerite.* The Wuuluman dolerite, which crops out in the Parish of Wuuluman, has been described by E. M. Basnett (1939). It is injected into the Upper Sedimentary Series, and consists of an altered dolerite intruded by a keratophyre magma, the original nature of the rock being partially or entirely masked by metamorphic and hybrid changes. The keratophyre has a sporadic distribution in the dolerite but is always surrounded by a zone of "spotted" hybrids which grade into the dolerite.

(iii) *Wuuluman and Yeoval Granites.* The Wuuluman granite, which intrudes strata of Silurian age, crops out to the east of Wellington in the Parishes of Wuuluman, Nanima, Bodangora and Wondaby and covers an area of about 47 square miles. It is a porphyritic, sphene-bearing, hornblende-granite which shows little differentiation. The phenocrysts of microperthite reach 4½ inches in length and often have an outer zone of green or white plagioclase. Well formed crystals showing simple twinning are abundant and smaller phenocrysts of green plagioclase also occur. Xenoliths are common throughout the granite mass and localised areas near the contact of the granite have been highly contaminated by shale and calcareous sediments. At Mt. Bodangora and in Por. 100, Par. Wondaby it has been strongly metasomatised, the felspar and the ferromagnesian minerals being replaced by flakes of mica and crystals of pyrites. Aplite and pegmatite dykes which occasionally contain tourmaline penetrate the contact zone and the edges of the granite. Dykes of granite-porphyry, quartz-bostonite, quartz-felspar porphyry and hornblende-porphyrite are also associated with the main intrusion. A small intrusion of hornblende-porphyrite on Poggy Creek is probably related to the Wuuluman granite.

Only a small portion of the Yeoval granite is included in the area under discussion. In the vicinity of Yeoval it is acid but not porphyritic and contains many large xenoliths of basic igneous rocks. At Walmer (north-east of Yeoval), where the intrusion is in contact with the Silurian andesitic rocks, it is a dark grey diorite and is probably a hybrid.

(iv) *Tertiary Intrusions.* The Tertiary intrusive rocks occur in the form of dykes and irregularly-shaped intrusions, while there is a probable Tertiary neck about five miles north-east of Wellington to the east of the Gulgong Road. The latter consists of a mass of brecciated Silurian rocks and some trachytic material, much of which has been replaced by hæmatite and calcite.

The dykes are all tinguaites, of which typical examples occur in Pors. 177 and 21, Par. Micketymulga, Por. 73, Par. Wuuluman, Por. 100, Par. Nanima, and Por. 10, Par. Nanima, just south of the Wuuluman-Gulgong Road junction. The groundmass is medium to fine-grained with strongly developed flow structure. Nepheline varies greatly in abundance and usually occurs in small idiomorphic crystals up to 0·5 mm. in diameter but may form poikilitic plates up to 2·5 mm. across. Analcite is present in the tinguaite from Por. 21, Par. Micketymulga. The pyroxene, which is often ophitic, is a sodic variety, and is deep green and strongly pleochroic. Orthoclase phenocrysts are rare.

The irregularly-shaped intrusion in Por. 121, Par. Ponto, is a syenite-porphyry which shows signs of considerable strain and has more orthoclase phenocrysts than groundmass. The groundmass is of granular orthoclase. Idiomorphic crystals of analcite up to 1 mm. across are often surrounded by a rim of bluish amphibole. Aegirine augite and arfvedsonite form irregular masses.

The dolerite intrusions in Por. 27, Par. Nanima, and Por. 19, Par. Wellington, are highly altered and therefore their Tertiary age is doubtful. The plagioclase has been strongly kaolinised and interstitial chlorite is abundant. Unaltered diopsidic augite is present in the rock from the former locality; the other contains felspar phenocrysts up to 5 mm. in length.

Structure.

The Lower Palæozoic rocks of the Wellington district have been folded into a series of plunging anticlines and synclines which are often asymmetrical but which trend in a north-west direction south of Wellington, changing to a northerly direction north of the town.

In the sections across the area an attempt has been made to illustrate the complicated folding of the Silurian and Devonian strata. West of the Catombal Range, however, dips are rare and outcrops are concealed beneath a covering of soil so that in this area the structure is more conjectural than in the east.

Throughout the Ordovician, Silurian and Lower and Middle Devonian strata there is much folding, while faulting and small overfolds are not uncommon, so that an estimation of actual thicknesses is impossible. The presence of four fairly large faults has been established, all being normal faults and occurring mainly in Silurian strata.

The Poggy fault (F_1–F_1) trends in a north-south direction and occurs to the west of Poggy Creek, where it has caused the tuffs and lamprophyre to be converted into schists (Basnett, 1942).

To the south is the east-west Wuuluman Fault (F_2–F_2) which passes from the Wuuluman Hills to the Poggy Fault. It is possible that this fault extends westward towards Wellington.

About five miles north-east of Wellington the Nobby fault (F_3–F_3) strikes in an east-west direction and dips to the north causing the sediments to crop out along the strike of the andesites. Minor folding and faulting due to the effect of drag is shown in a narrow bed of sandstone on the northern edge of the fault-block.

To the south-east of Newrea the Narragal fault (F_4–F_4) which dips to the south has resulted in a widening of the outcrops of Upper Devonian and Volcanic rocks. The fault is clearly exposed in Pors. 105, 141, Par. Narragal, where limestone abuts on slate and the rocks are contorted.

The relations between rocks of Ordovician, Silurian and Devonian ages are by no means clear. There appears to be a distinct unconformity between closely folded Ordovician cherts at Apsley and the surrounding andesites and limestone.

The indefinite nature of boundaries between Silurian and Lower and Middle Devonian rocks makes it difficult to determine the relations between them. There appears to be an overlap of Devonian limestone over the Silurian strata between Maryvale and Newrea, suggesting a slight difference in strike. Whether this change of strike occurs between Silurian and Lower Devonian or Lower Devonian and Middle Devonian it is impossible to say at present.

The Upper Devonian has a still more northerly strike than the underlying limestones so that there are probably three unconformities within the Lower Palæozoic here. They lie between

(i) Ordovician and Silurian,
(ii) Silurian and Lower or Middle Devonian.
(iii) Middle Devonian and Upper Devonian.

The last two are indicated by a slight change of strike.

Summary.

In the Wellington district, New South Wales, Silurian and Devonian rocks occur in a series of northerly-trending synclines and anticlines. The Silurian rocks have been separated into Sedimentary and Volcanic Series, and these occupy the greater part of the area mapped. To the west of Wellington the Catombal Range is formed of Lower and Middle Devonian limestones, overlain by resistant Upper Devonian sandstone, shale and conglomerate.

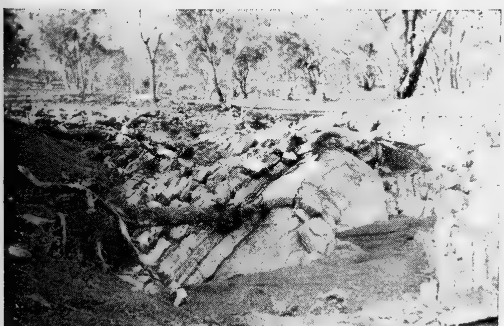
Granites intrude the Lower Palæozoic strata both in the north-east and south-west of the area and other minor intrusions of varied character occur.

1

4

2

5



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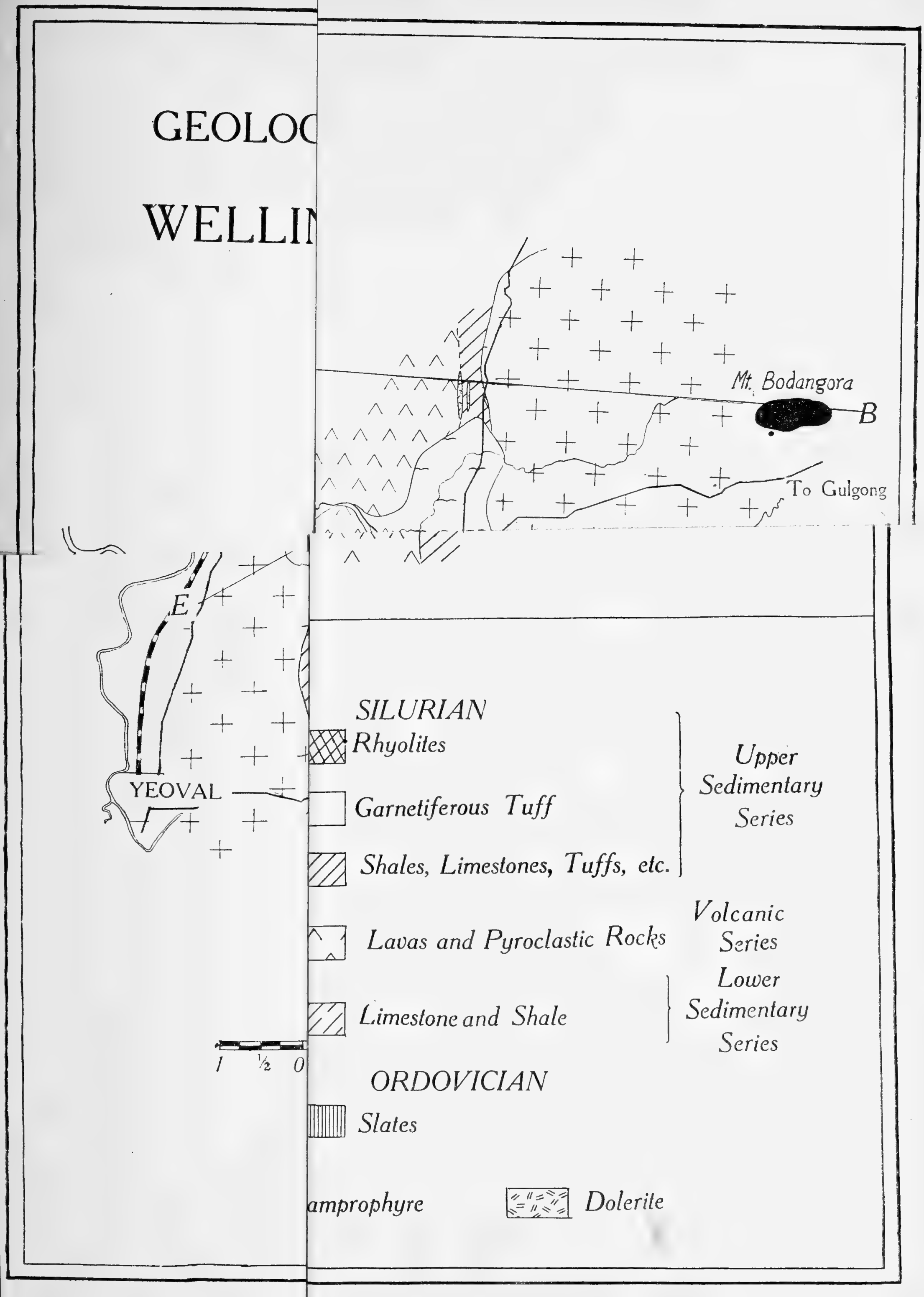
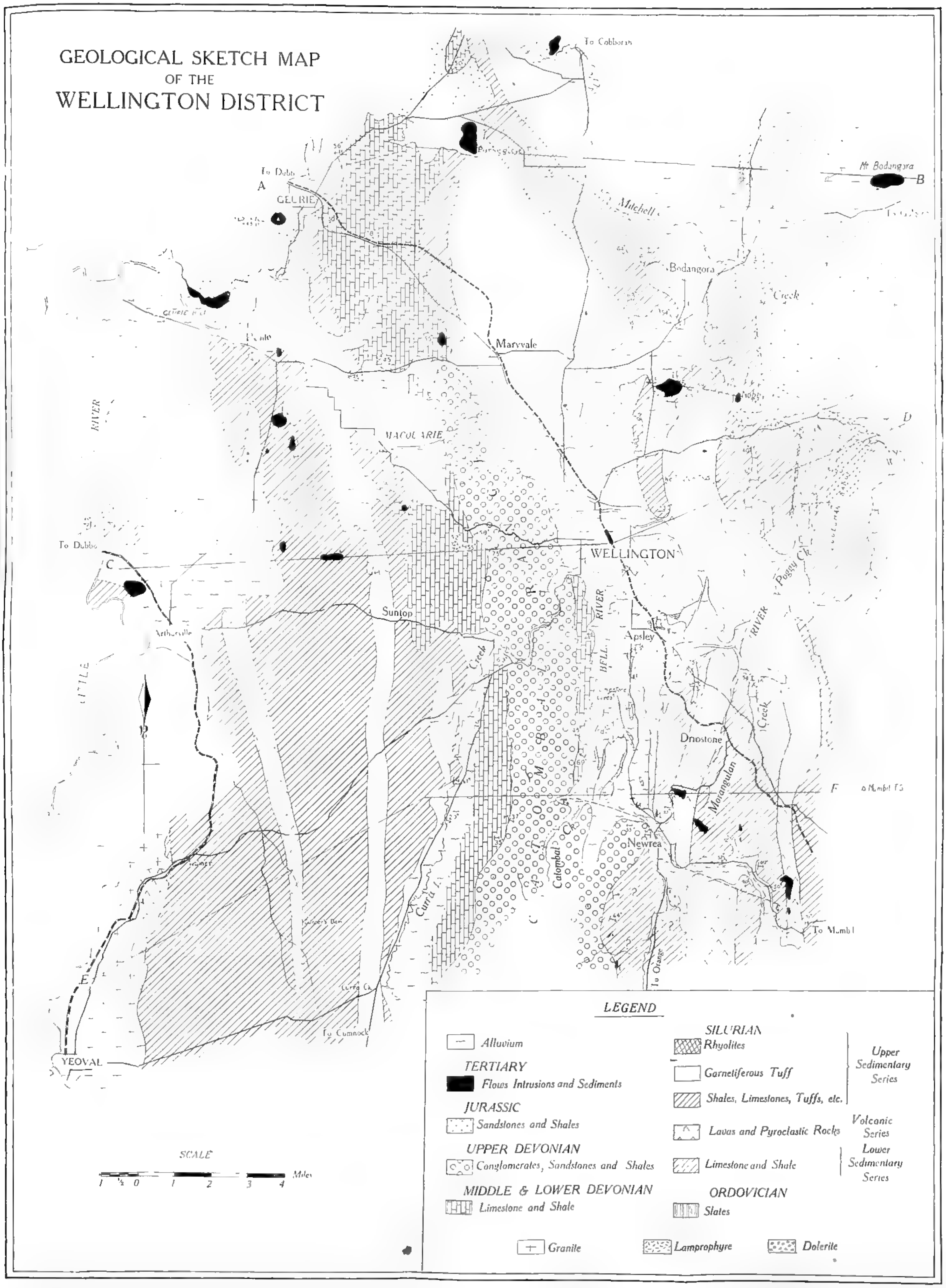
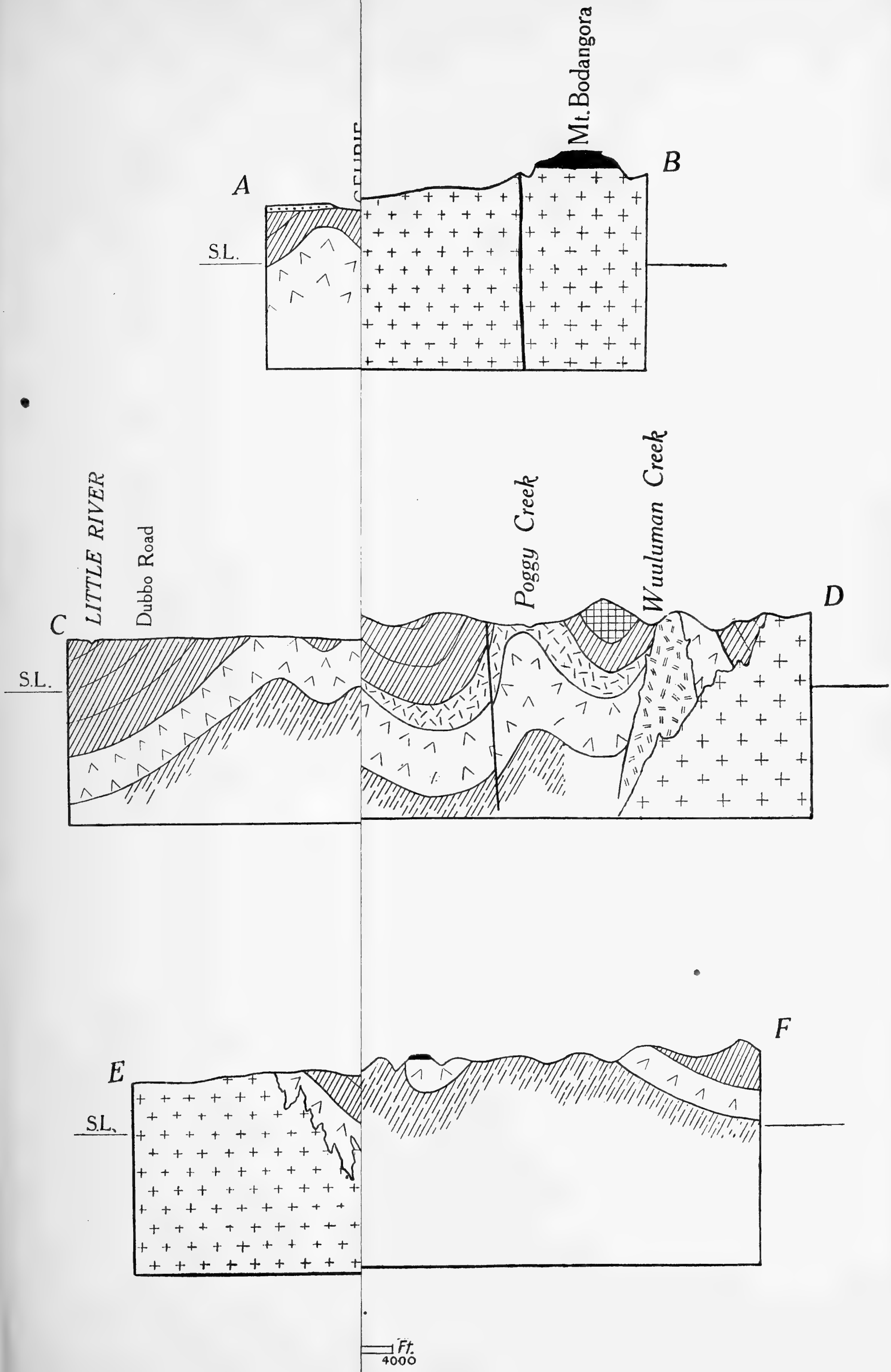

GEOLOG
WELLIN
Mt. Bodangora
B
To Gulgong
E
YEOVAL
SILURIAN
Rhyolites
Garnetiferous Tuff
Shales, Limestones, Tuffs, etc.
Upper Sedimentary Series
Lavas and Pyroclastic Rocks
Volcanic Series
Limestone and Shale
Lower Sedimentary Series
ORDOVICIAN
Slates
1 ½ 0
amprophyre
Dolerite


GEOLOGICAL SKETCH MAP
OF THE
WELLINGTON DISTRICT
To Cobborah
Mt Bodangora
B
A
GEURIE
Mitchell
Bodangora
Creek
Maryvale
RIVER
MACQUARIE
D
To Dubbo
C
WELLINGTON
Suntop
RIVER
BELL
Apsley
RIVER
Creek
Curra
Dripstone
Morangulan
Creek
F
Catombal Cr.
Newrea
To Mumbil
E
Curra Ck
To Cumnock
YEOVAL
To Orange
LITTLE
SCALE
1 ½ 0 1 2 3 4 Miles
LEGEND
Alluvium
TERTIARY
Flows Intrusions and Sediments
JURASSIC
Sandstones and Shales
UPPER DEVONIAN
Conglomerates, Sandstones and Shales
MIDDLE & LOWER DEVONIAN
Limestone and Shale
SILURIAN
Rhyolites
Garnetiferous Tuff
Shales, Limestones, Tuffs, etc.
Upper Sedimentary Series
Lavas and Pyroclastic Rocks
Volcanic Series
Limestone and Shale
Lower Sedimentary Series
ORDOVICIAN
Slates
Granite
Lamprophyre
Dolerite


Mt. Bodangora
A
B
S.L.
LITTLE RIVER
Dubbo Road
Poggy Creek
Wuuluman Creek
C
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S.L.
Ft.
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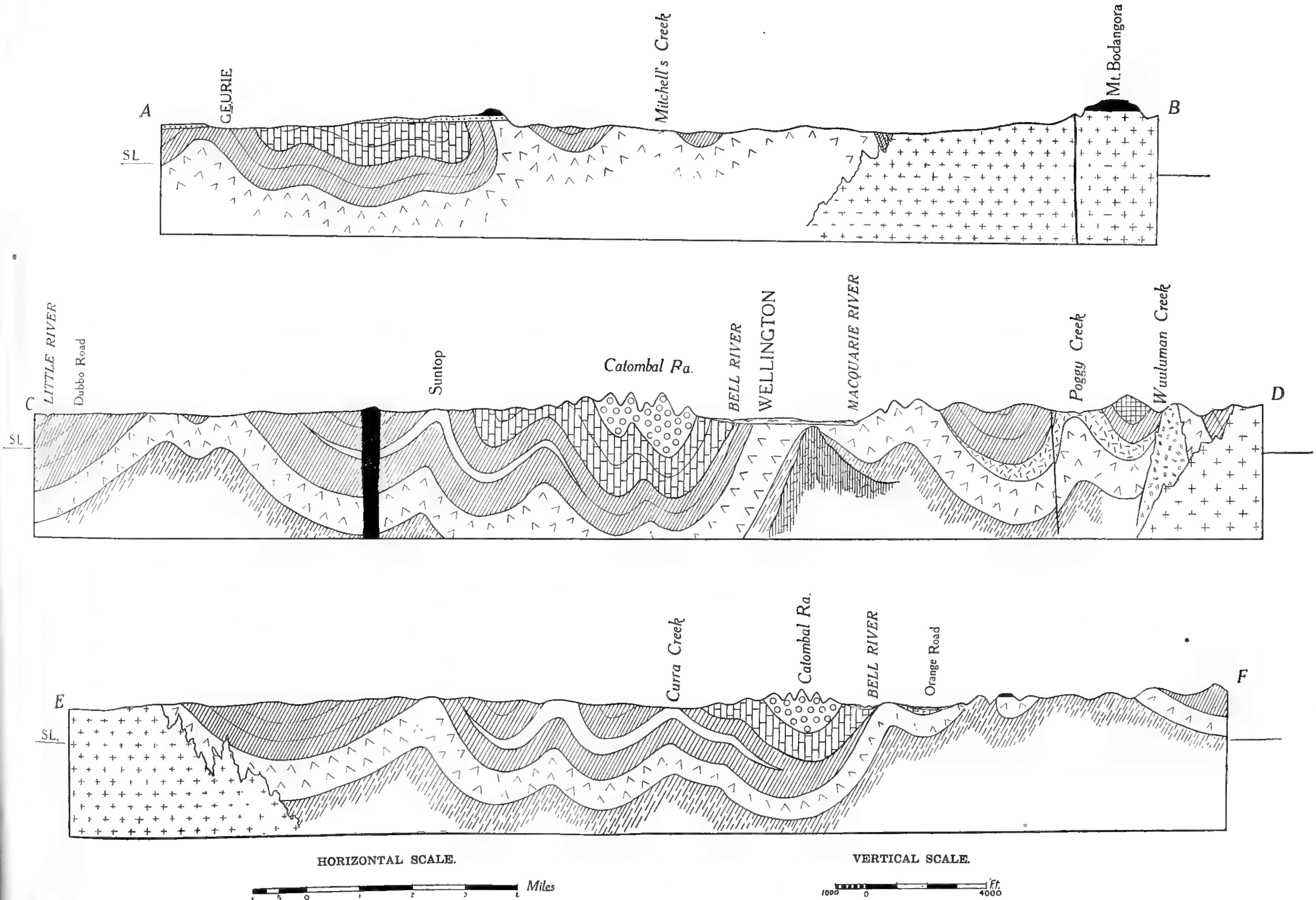
A
GEURIE
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Mitchell's Creek
Mt. Bodangora
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LITTLE RIVER
Dubbo Road
SL
Suntop
Catombal Ra.
BELL RIVER
WELLINGTON
MACQUARIE RIVER
Poggy Creek
Wuuluman Creek
D
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SL.
Curra Creek
Catombal Ra.
BELL RIVER
Orange Road
F
HORIZONTAL SCALE.
Miles
VERTICAL SCALE.
1000
0
4000
Ft.

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Explanation of Plate I.

Fig. 1.—Ordovician cherts on the Mudgee Road 1½ miles from Wellington.

Fig. 2.—A boulder of Silurian andesite on the Cobbora Road five miles from Wellington. Xenoliths of andesitic lavas occur in a matrix of andesite.

Fig. 3.—Characteristic minor folding in Middle Devonian limestones south of the Wellington Caves.

Fig. 4.—A rugged outcrop of Upper Devonian conglomerate on Curra Creek, three miles from Wellington on the Parkes Road. The conglomerate is banded with sandstone and shale.

Fig. 5.—Ferruginous grit of probable Jurassic age on Mt. Bodangora. It overlies metasomatised granite containing felspar phenocrysts. Basalt flows lie above the grits.

Fig. 6.—Looking north across the Macquarie Valley from Suntop (west of the Catombal Range). Most outcrops are covered by alluvium but a Tertiary intrusion at Barren Rock forms a bold feature.

ISSUED JUNE 19, 1946

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VOLUME LXXIX

PART II

DETERMINATION OF THE BOILING POINTS OF HYDROGEN CHLORIDE SOLUTIONS.

By L. M. Simmons, B.Sc., A.A.C.I.,
The Scots College, Sydney.

Communicated by Dr. F. Lions.

With two text-figures and two tables.

Manuscript received, April 18, 1945. Read, June 6, 1945.

The International Critical Tables list the boiling points of solutions of hydrogen chloride in water having concentrations up to M%HCl$=26 \cdot 3$ based on the work of Carrière and Armand (1924). This list gives the constant boiling mixture at 760 mm. pressure as having M%HCl$=10 \cdot 5$ and b.p. $109^\circ \cdot 7$ C. According to the very careful measurements made by Bonner, Foulk, Hollingsworth, Hulett, Titus and Wallace the constant boiling mixture at 760 mm. pressure contains $20 \cdot 23 \pm 0 \cdot 01$ per cent. by weight of HCl, i.e. M%HCl$=11 \cdot 1$, and boils at $108^\circ \cdot 584$ C. (Bonner and Wallace, 1930) values which are inconsistent with the list given by the International Critical Tables.

The methods for determining boiling points used by Bonner and others (*loc. cit.*) are unsuitable for other than pure substances and constant boiling mixtures, and an examination of the usual methods for determining boiling points discloses that up to the present no rapid, easy and precise method exists for both pure substances and all their mixtures.

The method used in the present investigation was designed to determine the boiling point to $\pm 0 \cdot 1$ centigrade degree of any pure liquid or liquid mixture which has negligible effect on glass, mercury and selected lubricant. Only small quantities (about one-third ml.) are required. Unreliable corrections for emergent column and for variation in atmospheric pressure (Young, 1922) are eliminated and the composition of the liquid cannot appreciably alter other than by decomposition during the measurement. The time needed for each b.p. determination is less than half an hour, of which only about ten minutes absorb the investigator's attention.

Experiments are at present proceeding on (*a*) the elimination of the tap lubricant, (*b*) application to liquids which attack mercury, (*c*) a method of mixed boiling points to parallel the well-known mixed m.p. technique applied to solids, (*d*) an application to the ebullioscopic determination of molecular weights.

Results.

The results obtained for hydrochloric acid by the present method are shown by curve A (Fig. 1) and were plotted from the readings shown in Table 1.

For the purpose of comparison, Fig. 1 also shows a curve drawn according to the data given in the International Critical Tables (curve B).

It will be seen that the boiling point given by the International Critical Tables for the constant boiling mixture at 760 mm. is more than a centigrade degree higher than that given by Bonner *et al.* (*loc. cit.*) and that all mixtures were stated to have higher boiling points than those obtained by the present method up to about 24 per cent. by weight of HCl. The two curves become identical above 28 per cent. HCl by weight.

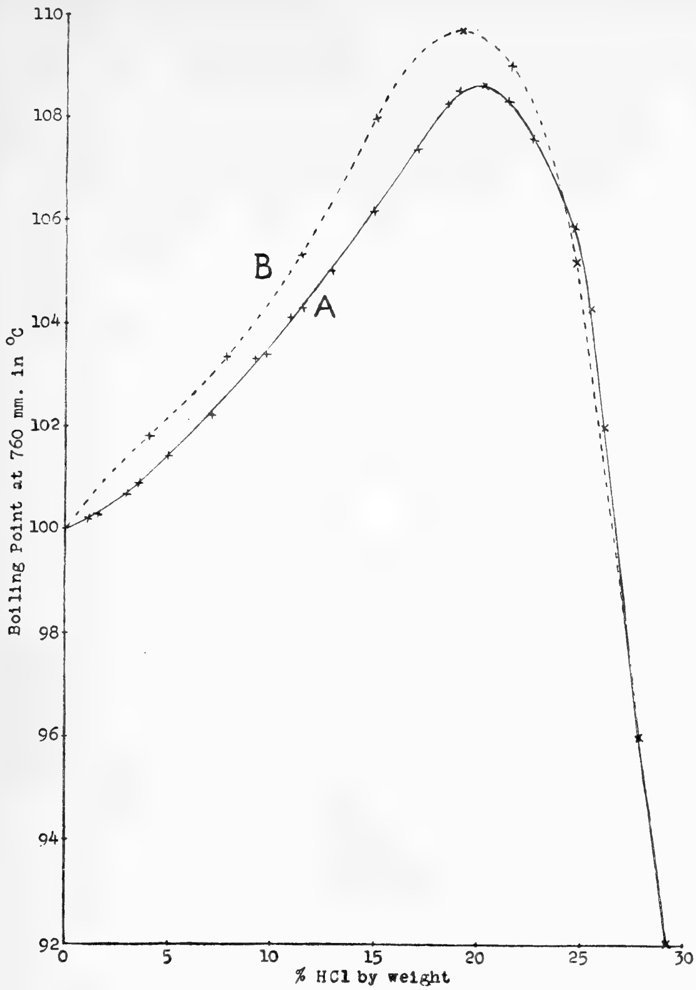

Fig. 1.—The Boiling Points of Hydrochloric Acid.

A. According to the present investigation.
B. According to the International Critical Tables.

TABLE I.

The Boiling Points of Hydrochloric Acid containing Various Percentages by Weight of HCl at a Pressure of 760 mm.

% HCl by Weight.	b.p. ° C.	% HCl by Weight.	b.p. ° C.	% HCl by Weight.	b.p. ° C.
0·0	100·0	9·6	103·4	20·2	108·6
1·0	100·2	11·0	104·1	21·5	108·3
1·5	100·3	11·5	104·3	22·8	107·6
2·9	100·7	12·9	105·0	24·7	105·9
3·5	100·9	14·9	106·2	25·5	104·3
4·9	101·4	17·1	107·4	26·1	102·0
7·0	102·2	18·5	108·3	27·9	96·0
9·1	103·3	19·0	108·5	31·4	85·3

Table 2 is therefore submitted to replace that given on page 309 of Volume 3 of the First Edition of the International Critical Tables :

TABLE 2.

Aqueous Mixtures.

B=HCl.

b.p. °C.	M%B.
100·0	0·0
101·1	2·0
102·6	4·0
104·3	6·0
106·2	8·0
108·3	10·0
108·584	11·1
108·3	12·0
105·8	14·0
92·0	17·0
82·7	18·5
19·0	26·3

The last two entries in Table 2 have not been checked by the present method.

APPARATUS AND PROCEDURE.

The W-tube shown in Fig. 2 is made of soda-glass having an internal bore of about 7 mm. Overall length of the limbs is about 15 cms., and a tap divides the middle limb A into two approximately equal parts. Each limb is graduated in millimetres from a datum line perpendicular to

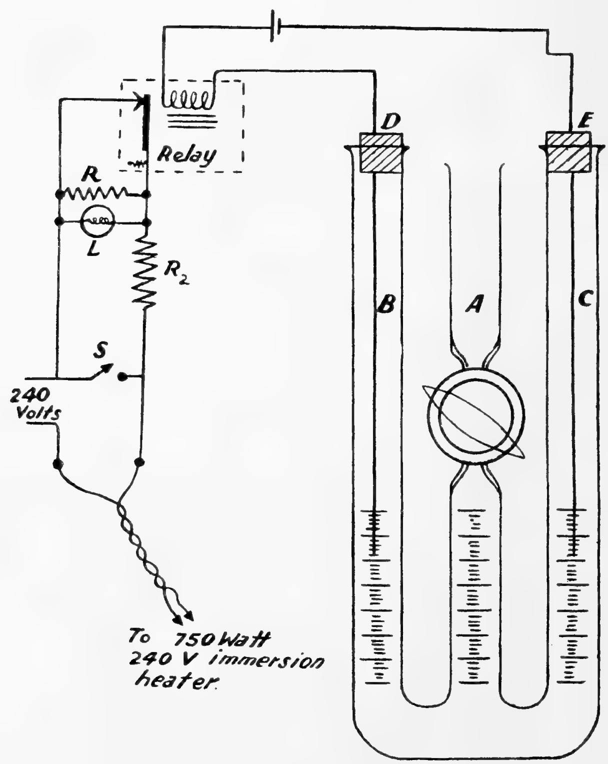

Fig. 2.—Boiling Point Apparatus.

the axes of the limbs near the bends to a similar line just below the tap. In the following description the graduations nearest the bends will be referred to as O.

The tube is cleaned and dried in an oven. After cooling in the air the tap is lightly lubricated with a non-volatile grease which does not dissolve in hydrochloric acid. Mercury is poured down one of the outer limbs B or C with the tap open until the mercury stands at about the positions occupied by the letters A, B and C in Fig. 2. During the filling the tube is gently tilted from time to time to prevent bubbles of air being entrapped.

The tap is then turned off and a straight narrow tube connected through a trap to a filter pump is lowered into one of the outer limbs B or C so as to remove mercury from the apparatus until the levels in B and C are just below 0 ; the level in the middle limb remains at A because the tap is turned off. The test liquid whose boiling point is to be determined is poured into the open end of A until it forms a layer about 1 cm. high above the mercury. It is generally found that a tiny bubble of gas tenaciously adheres to the apex of the mercury meniscus ; this is removed by lowering a narrow open tube through the acid into the mercury so that it encloses the bubble. The upper end of the narrow tube is then closed by the finger and the bubble removed together with some acid and mercury.

The tap is cautiously turned on to allow the mercury to flow ; it is firmly turned off when a layer of acid about 3 mm. high is between the mercury and the bottom of the tap.

The tube is clamped with its limbs vertical in a large beaker nearly filled with Paraffin B.P (or other high-boiling liquid). the open ends of the limbs being three or four centimetres above the surface of the oil. A small plumb-line lowered down one of the outer limbs ensures that they are vertical. In this position the mercury levels in the outer limbs stand at similar graduations.

A mechanical stirrer and a 750-watt 240-volt immersion heater are immersed in the oil. A short-stem mercury thermometer graduated in fifths of centigrade degrees is clamped so that its bulb is close to the middle of the lower part of the middle limb and so that the part of the thermometer scale to be used is totally immersed in the oil.

The grooved corks D and E (Fig. 2) bearing steel knitting needles as electrodes are inserted in the open ends of limbs B and C. The corks do not prevent ingress or egress of air. The electrodes can be raised or lowered manually through the corks and are connected to the relay circuit shown in Fig. 2. The exact positions of the lower ends of these electrodes will be determined later ; at the present stage they are roughly half-way up the millimetre scales.

Stirring is started and the switch S closed so that the heater is directly connected to the 240-volt supply. This rapidly raises the temperature of the bath to within about 5 degrees of the expected boiling point of the sample. Switch S is then opened, thus placing the variable resistance R_2 in series with the heater. The resistance of R_2 is adjusted until the rate of heating of the oil is about one-third of a centigrade degree per minute. The value of this resistance is not critical ; in the present case it was found to be about 110 ohms.

At this stage the oil temperature is slowly rising and some vaporisation of the sample has occurred, causing the mercury below the tap to drop so that its meniscus lies on the millimetre scale. Let its present position be a mm. above 0 and let the mercury in limbs B and C now be at the b mm. graduations. Further, let a mercury barometer having a brass scale correct at 0° C. read h mm. at air temperature t° C. Then the corrected barometric pressure in Sydney and suburbs will be $\mathrm{H}=h-\frac{1}{8}t-0{\cdot}001h$ mm. to the nearest mm. The electrodes D and E are adjusted so that their lower ends are at the graduations $\dfrac{760-\mathrm{H}+a+2b}{3}$ mm.

As the temperature continues to rise the mercury rises in limbs B and C until it touches the electrodes, thus completing the relay circuit. The armature is attracted and the variable resistance R is brought into series with the heater and R_2. The value of R is not critical but is adjusted so that the oil temperature falls at about one-third of a centigrade degree per minute. With the present apparatus this was obtained when $\mathrm{R}\doteqdot 40$ ohms. The fall in temperature causes the vapour to start condensing and the mercury in the outer limbs falls, breaking the relay circuit and causing the temperature of the oil to rise. The flashing of the pilot lamp L announces this state of affairs to the investigator who then makes any necessary final adjustments to the height of an electrode to ensure that at make or break of contact the meniscus in A is 760 − H mm. below or above the menisci in B and C according to whether H is less or greater than 760 mm.

It is found from then on that the difference in mercury levels does not vary by more than 1 mm., and that the temperature of the oil does not vary by more than $0 \cdot 2$ centigrade degree. The temperature is read for several consecutive movements of the relay, and the resulting temperature readings are found to agree to within one-tenth of a degree. The thermometer is read through the oil with the aid of a reading glass.

As an example, let the air temperature be 20° C. and the barometer having a brass scale correct at 0° C. read $745 \cdot 65$ mm. at Sydney. Corrected barometric pressure $H=745 \cdot 65-\frac{20}{8}-0 \cdot 75=742 \cdot 4$ mm. Let the mercury in the middle limb stand at 31 mm. when in the outer limbs it stands at 7 mm. Then the electrodes should be adjusted to $\frac{760-742 \cdot 4+31+14}{3}=20 \cdot 9$, i.e. to the 21 mm. marks. Final adjustment would be made to ensure that the mercury in the outer limbs touches the electrodes when the mercury in the middle limb is between 17 and 18 mm. lower than in the outer limbs. The mercury levels would probably be 21 mm. in the outer limbs and 3 mm. in the middle limb. The pressure of the vapour in the middle limb is then 760 mm. to the nearest mm.

Since the height of the layer of sample liquid in the middle tube was of the order of 3 mm., and the height of the column of vapour above it was of the order of 30 mm., the ratio of the volume of liquid to volume of vapour is of the order 1 : 10. The mass of the vapour would therefore be about one-half per cent. of the mass of the liquid sample. Hence it is claimed that the present method minimises changes in composition of the sample during the determination.

Standardisation of the Thermometer.

The thermometer was tested by the Standards Laboratory, Sydney, over the range 95° C. to 110° C. for total immersion to an accuracy of $\pm 0 \cdot 05$ centigrade degree. The reported corrections all lay within those limits.

Preparation of Solutions of Hydrogen Chloride.

Constant boiling hydrochloric acid was prepared under known atmospheric pressure by distillation according to the method described by Hulett and Bonner (1909). It was stored in a pyrex flask because it was found that the acid dissolved sufficient soda-glass in a month at room temperature ($20 \cdot 25$° C.) to raise its b.p. by $0 \cdot 2$ centigrade degree. Weighed quantities of distilled water and constant boiling acid were mixed to produce the various solutions up to $20 \cdot 2$ per cent. HCl by weight. The more concentrated solutions were prepared by mixing analytical reagent concentrated hydrochloric acid with the constant boiling acid, the concentrations of such mixtures being determined by titration with NaOH (standardised against the constant boiling acid) using screened methyl orange and weighing the acid titres.

Summary.

A method has been devised for the rapid determination of the boiling points of pure liquids and liquid mixtures which do not attack mercury, glass or selected tap lubricant, to within $0 \cdot 1$ centigrade degree. The method obviates recourse to calculated corrections for emergent column and variations in atmospheric pressure, requires about $0 \cdot 3$ ml. of liquid, prevents sensible variations in composition of the liquid phase and avoids superheating. The method has been used to correct the list of boiling points of hydrochloric acid appearing in the International Critical Tables.

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CONTACT POTENTIAL DIFFERENCE AS A TOOL IN THE STUDY OF ADSORPTION.

By R. C. L. Bosworth, M.Sc., D.Sc.(Adel.), Ph.D.(Cantab.), F.A.C.I., F.Inst.P.

Manuscript received, April 30, 1945. Read, June 6, 1945.

I. Introduction.

The fact that the presence of a film too thin to be visible could profoundly modify the contact p.d. between any pair of metals was first recorded by J. Erskine Murray (1898). Murray used the method of measurement introduced by Lord Kelvin (1898). This method depends on the fact that if the plates of a condenser are made of different metals they will normally contain a charge sufficient to maintain an e.m.f. across the condenser equal to the contact p.d. of the two metals, and that if the plates of the condenser are separated and the capacity thereby changed, a current must necessarily flow in order to maintain an e.m.f. equal to contact p.d. With the modern realisation of the tenacity with which metal surfaces hold primary gaseous films and the great difficulty with which these films are removed and a pure metal surface thus produced, we now prefer some method of measurement in which metal filaments take the place of Kelvin's plates. These metal filaments can of course readily be outgassed through heating to a high temperature by means of an electric current; provided the metals chosen have sufficiently high melting points. Special methods have been described in the literature for dealing with the more fusible metals by depositing them over a core of a more infusible one.

Reimann (1935) has described one of the most satisfactory methods for comparing the contact p.d.'s of pure metals. Two loop filaments were arranged to hang with the tips far closer together than the other portions. One of the filaments was maintained at a high temperature and acted as a source of electrons; the second, or cold filament, acted as the anode and the electron current flowing to it was measured and plotted as a function of the external voltage applied between the two filaments. When a film was formed over the surface of the cold filament its surface potential was changed, thereby changing that potential difference between the filaments which was effective in drawing electrons to the cold filament from the hot one, namely the sum of the contact p.d. between these filaments and the externally applied p.d. Consequently when the curve electronic current versus external voltage was again plotted, the curve obtained was parallel to the first, and could be made identical with the latter by giving it a voltage displacement equal and opposite to the contact potential difference. It is important to realise that this method measures the c.p.d.'s between the same material surface in two different stages of chemical contamination, and accordingly the method is particularly useful in the study of adsorption problems.

II. Experimental.

In a modification of the apparatus above adopted by Bosworth and Rideal (1937) an arrangement of the skew filaments at right angles was employed as it was found that such an arrangement could be made mechanically more stable and rigid. The two skew filaments were connected to two independent electric circuits carefully insulated from one another. Either filament could be heated to any desired temperature. The leads to each filament external to the vacuum tube

containing the filaments were connected by resistances in parallel to the filaments. Each resistance had a variable centre point: the galvanometer measuring the electron current was connected across these centre points.

The circuit used is illustrated diagrammatically in Figure 1. The bulb B contains the two cross filaments of tungsten F_1 and F_2 and is exhausted via the side tube S. The external circuit of F_1 consists of the parallel resistance r_1 with variable centre point P_1, series variable resistance R_1, commuting switch S_1, battery C_1 and ammeter A_1. The external circuit of F_2 consists of the two corresponding resistances r_2 and R_2, switch S_2, battery C_2 and ammeter A_2. The galvanometer G is connected from P_1 to P_2. The potentiometer Q provides a source of variable external p.d. The two filaments are carefully aged and outgassed. Filament temperature versus current

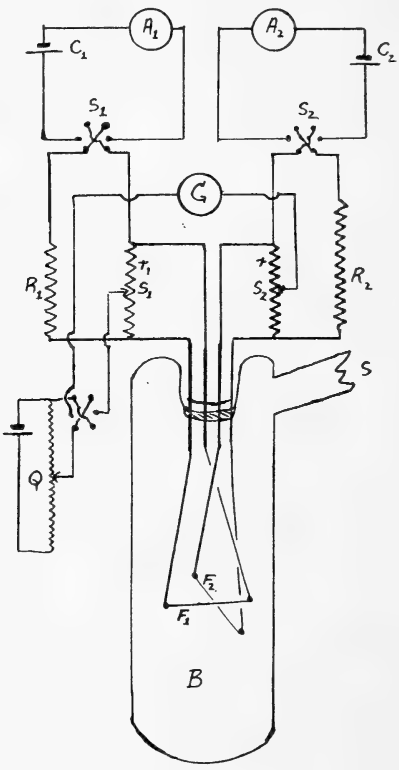

Figure 1.

curves are drawn for each. Filament F_1 is now heated to about 2500° K. and the galvanometer read, preferably at zero applied external p.d. The commuting switch S_1 is then used to reverse the current in F_1 and if the galvanometer changes the point P_1 is not at the same potential as the effective point on F_1 which is acting as the electron source. The point P_1 is therefore adjusted until the galvanometer reading is unchanged when S_1 is switched across. Following this adjustment, filament F_2 is now heated to about 2500° K. and P_2 similarly adjusted until the galvanometer reading is independent of the position of the switch S_2. (Filament F_1 can either be turned off or left on during this adjustment.)

In operation filament F_1 was used as the emitter filament and operated at 2500° K. Filament F_2 was used to study the behaviour of adsorbed films and was normally operated at some much lower temperature, usually 300° K. After long outgassing at the highest vacuum obtainable, both surfaces were flashed at 2800° K. and obtained in a clean state. In this state the current-volts curve was drawn by plotting the galvanometer reading against the voltage applied from

the potentiometer Q. Usually the voltage was varied from about -4 to $+2$ volts. Oxygen at a pressure of about 10^{-4} mms. of mercury pressure was then admitted momentarily and then pumped out again. Any oxygen film forming on the emitter filament is rapidly evaporated off again, but a complete film remains on the cold filament, and when the current-volts curve is measured again, the second curve will be found to be parallel to the first. When the outgassing was sufficiently prolonged this displacement proved to be unchanged by further treatment and

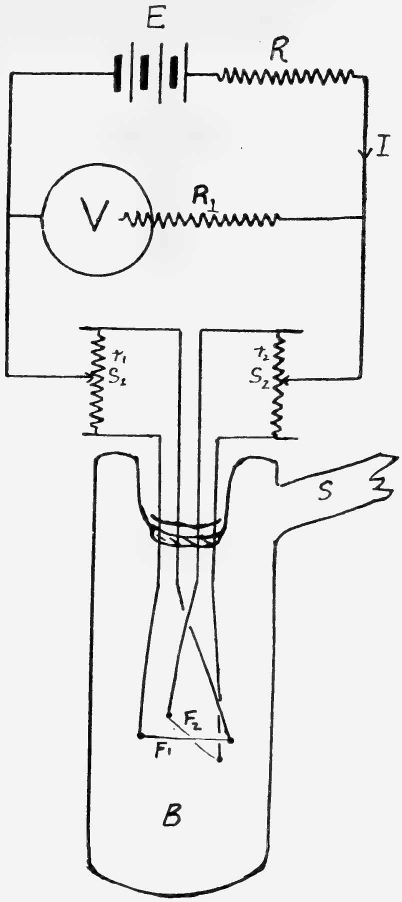

Figure 2.

to be equal to $+1 \cdot 78$[1] volts—meaning that after forming the oxygen film the applied voltage must be increased by $1 \cdot 78$ volts to restore the current to its original value. $-1 \cdot 78$ volts is therefore the contact potential difference between clean tungsten and tungsten covered with oxygen. This figure was used to check new experimental tubes and operating conditions throughout this work.

Since the current-volts curves for different conditions of the cold filament are all parallel, it is necessary only to draw this curve once with any given experimental set-up, and then choose a suitable voltage and measure only a single current value at any given filament condition, and calculate from the curve above the c.p.d. corresponding to this current. This single measurement method permits transient chemical phenomena at the surface to be investigated. The strongly curved nature of the current-volts characteristic of this type of tube has two consequences of

[1] Reimann (1935) obtained a figure of $1 \cdot 70$ for this same quantity.

manipulative importance. In the first place the tube is a good rectifier of all A.C. disturbances. Spurious readings can result from such disturbances, and consequently when working in city areas it is most desirable to screen the tube with an earthed shield. The filament leads are also preferably encased in earthed composition tubing.

When using the constant external voltage method, the curved characteristic also results in great changes in sensitivity as the c.p.d. of the surface changes. Having in mind this difficulty the circuit illustrated in Figure 2 was devised, in which a reading directly proportional to the c.p.d. is obtained. In this arrangement a battery of e.m.f. E feeds a current I through the resistance R and the c.p.d. tube, the negative going on to the centre tap of the emitter filament F_1 and the positive lead going on to the corresponding centre tap of the collector filament F_2. The potential difference across the c.p.d. tube is read by the voltmeter V of resistance R_1. This voltmeter will normally consist of a sensitive galvanometer with R_1 in series. The resistance R is chosen sufficiently large to control the current I, as well as the current through the tube, at practically a constant value independent of any changes in the c.p.d. tube. Consequently the reading of V in volts is equal and opposite to c.p.d. between the filaments. R and E are conveniently chosen so that V reads zero when the two filaments are in the same state. Detailed analysis of the circuit equations have shown that with ordinary construction of the c.p.d. tube a suitable value for the battery voltage E is 24 volts.

The behaviour of surface films at elevated temperatures has been studied by operating the c.p.d. tube with both filaments heated. Trouble is, however, experienced with interpretation of the results whenever the thermionic emission of the cold filament ceases to be negligibly small in comparison with the hot. Generally speaking the cold filament should be at least 600° C. colder than the hot. Larger temperature differences are desirable if strongly positive films are present on the cold filament; however, all such films so far studied are quite unstable even 1000° C. below 2500° K.

III. Some Properties of Electro-positive Films.

When a tungsten surface is exposed to the vapours of the alkali metals electro-positive films are built up on the surface. The contact p.d. between the covered surface and the original bare surface increases to a maximum (usually when the surface is about 70% covered), and thereafter decreases asymptotically to the value appropriate to the bulk alkali surface. With the simple equipment described above all changes in surface concentration up to the maximum c.p.d. value can therefore be studied. The author has described a three-filament tube which permits a study of films of all concentrations (Bosworth, 1938). Briefly, the concentrated film is formed of one filament, and when a measurement of the surface concentration is required, a parallel filament is flashed to clean it, its c.p.d. with respect to a perpendicular hot filament is measured, and then the filament with the concentrated film is flashed and the c.p.d. change in the parallel filament recorded. From the geometry of the tube the fraction of the atoms evaporated from the first filament incident on to the second could be calculated. The distance apart of the filaments was so adjusted that the concentration on the second filament was not raised above the maximum c.p.d. value.

Evaporation of surface films has been studied by raising the collector filament to a predetermined temperature, holding it at that temperature and observing the rate of change of c.p.d. Rate of evaporation varies just as much with surface concentration as with temperature. In general the more concentrated films evaporate more rapidly than the more dilute. In the special case of sodium on tungsten films, which have been closely studied, there appears to be a range of temperatures for which films more concentrated than $\theta=0\cdot4$ are unstable and tend to separate into dilute films and patches of bulk sodium. The heat of evaporation calculated from the temperature coefficient of the rate of evaporation by means of the Clapeyron equation, varies with the film concentration and has a minimum at some particular value of θ. The symbol θ is used

to denote the fraction of the surface covered with one molecular layer. For a complete monolayer $\theta=1$, for two complete layers $\theta=2$, etc.

Table I below gives the variation with θ of the c.p.d. and the heat of evaporation for sodium films. The figures are taken from papers by the author (1937, 1938).

TABLE I.

θ	C.p.d. in Volts Against Tungsten.	Heat of Evaporation in Calories per Mole.
0·0	0·0	32,000
0·15	1·56	28,500
0·30	2·04	27,000
0·45	2·51	23,000
0·60	2·68	20,000
0·75	2·78	17,000
1·0	2·64	20,000
1·5	2·52	23,000
2·0	2·49	24,000
10·0	2·48	24,000

It will be observed that there is a fairly close parallelism between the heats of evaporation and the contact potential differences.

IV. Measurement of Vapour Pressure by the C.P.D. Method.

Frovided that we can assume a definite fraction of the atoms incident onto a surface stick to that surface and go to build up an adsorbed film, the contact p.d. method provides a very sensitive and general method for measuring partial vapour pressures. The method was first studied by exposing a filament to a saturated sodium vapour at different temperatures and measuring the rate at which the film is built up. The time τ taken by the film in attaining a c.p.d. corresponding to a given fraction θ of the surface covered is given by the relationship

$$\frac{1}{\tau}=7\cdot35\times10^{7}\ \frac{\alpha p}{\sqrt{MT\theta}}\ \text{reciprocal seconds} \quad \ldots\ldots\ldots\ (1)$$

where p is the required vapour pressure, T the absolute temperature, M the molecular weight (23 in the case of sodium vapour) and α the condensation coefficient or the fraction of the molecules incident on to the surface which stick to it. α may be found by measuring τ under conditions where p is either known or measurable by other means. For sodium α proves to be unity. By means of equation (1) partial pressures of sodium vapour as low as 10^{-11} mms. of mercury may readily be measured.

Once the appropriate value of α has been determined this method may be used for very low pressures of such gases as oxygen, hydrogen and nitrogen which give electro-negative films on tungsten.

V. Properties of Electro-negative Films.

When a clean tungsten filament is exposed to an electro-negative gas at a low pressure a negative film builds up at first rapidly and then more and more slowly, tending finally to a value characteristic of the film.

It has been shown that in the formation of these films atoms incident on to the surface only condense when they strike a surface lattice point which is bare. Now molecules of oxygen, hydrogen and nitrogen are diatomic, while on the surface they are adsorbed as atoms and not molecules. One condition for condensation therefore requires that the incident molecule strike two neighbouring bare spaces on the surface. Working from this assumption, J. K. Roberts (1937) argued that if the film formed be immobile the process of condensation will leave finally a number of isolated single spots completely surrounded by adsorbed atoms and on which condensation is impossible, and was able to show that θ for the final state of the surface would only be 0·92. On the other hand were the film formed mobile, then as soon as one molecule condenses we may expect that the two adatoms[2] formed will tend to move apart until when θ=0·5, or the surface is half covered, the most probable state of the film will be one in which every second lattice point is occupied. A complete distribu-

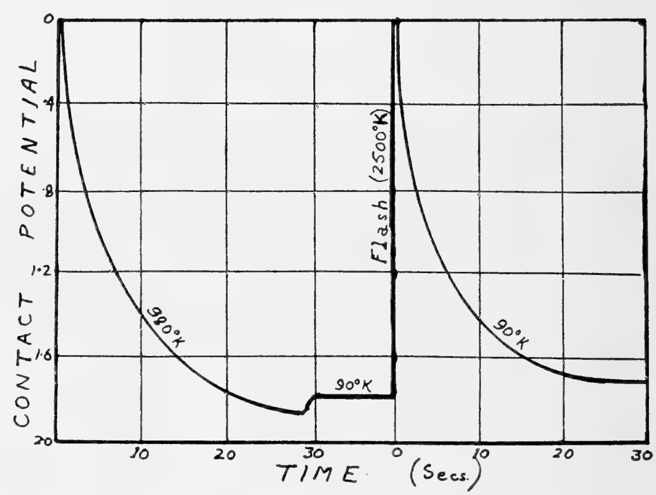

Figure 3.

tion of this type, however, would mean that condensation would stop at this point. In practice, however, thermal agitation on the surface tends to break up the orderly arrangement the more the less the repulsive forces acting between the adatoms. The actual behaviour to be expected therefore is that condensation will commence to proceed more slowly than for the corresponding immobile film at values of θ greater than 0·5. Since the actual rate of condensation depends on the ratio of the mean thermal agitation to the repulsive potential energy on the surface it is to be expected that this rate will increase as the temperature increases. Furthermore condensation now proceeds to completion. The curve for mobile condensation, as calculated by Roberts (1937), after falling below the curve for immobile condensation at about θ=0·4, cuts the latter curve again at about θ=0·9.

Most films formed at low temperatures are immobile and many acquire the property of mobility on heating. An experiment was therefore directed towards studying the difference between the rate of condensation of oxygen on tungsten at liquid air temperature (90° K.) and 980° K., it having previously been shown that at the latter temperature the film was completely involatile. Figure 3

[2] The words "adatom" for adsorbed atom and "adion" for adsorbed ions was first used by I. Langmuir.

represents the results obtained. The filament in the presence of oxygen gas at a pressure of 3×10^{-6} mms. of mercury was flashed at 2500° K. to clean the surface from all adsorbed films and the temperature was dropped to 980° K. and the change in contact potential followed for 30 secs. as condensation proceeded. In 30 seconds the filament had acquired a potential of $-1 \cdot 84$ volts relative to the clean state at 90° K. On dropping the temperature further to 90° K. for 10 seconds the potential rose to $-1 \cdot 76$ volts. This small change is due to the fact that the work function of a WO surface has a positive temperature coefficient. $-1 \cdot 76$ volts therefore represents the contact p.d. against clean tungsten of the film of θ value formed in 30 secs. at 980° K. and measured at 90° K. Following the treatment outlined above the film was again flashed to clean it and the condensation studied at 90° K. As Figure 3 shows, the final potential acquired in this case was only $-1 \cdot 65$ volts, which would therefore appear to correspond to a final film for which θ is less than $1 \cdot 0$, on the assumption later to be justified, that θ is directly proportional to the c.p.d.

In further studies of the condensation of oxygen on tungsten a steady low pressure of oxygen was provided by coating the inside of the bulb of the vacuum tube with a mirror of metallic sodium and immersing the bulb in liquid air. By this means the sodium vapour pressure was made utterly negligible and a condition attained in which any oxygen molecule incident on to the walls is not reflected. A steady stream of oxygen at a regulated rate was then provided by heating a subsidiary nickel filament which had been coated with a layer of barium peroxide. The oxygen pressure attained was then directly proportional to the rate of dissociation of the BaO_2 and could thus be controlled in terms of the temperature of the source. The BaO_2 filament may be most conveniently prepared by dipping a nickel filament in molten $Ba(OH)_2.8H_2O$. The filament with its adhering layer is then strongly heated in a high vacuum to drive off all the water and cooled gradually (by slowly cutting out the heating current) in an atmosphere of oxygen.

The theory proposed by Roberts for the formation of an immobile film from a diatomic gas leaves unspecified the condensation coefficient α_2 or the ratio of the number of effective collisions with the surface to the number of molecules condensing. The equation for the rate of formation of the film is given as

$$\int_0^\theta \frac{d\theta}{(1-\theta-0 \cdot 1117\theta^4)^2} = \frac{2\alpha_2 p_2 t}{N_S \mu_2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where $\mu_2 = \sqrt{2\pi mkT}$

p_2 is the partial pressure due to the molecules,
m is the mass of the molecules concerned,
k is the Boltzmann gas content,
T is the absolute temperature, and
N_S is the number of spaces on unit area of the surface available for adsorption. In the case of tungsten $N_S = 1 \cdot 424 \times 10^{15}$.

Equation (1) may be written in the form

$$R(\theta) = \frac{2\alpha_2 p_2 t}{N_S \mu_2}$$

or

$$\theta = I\left(\frac{2\alpha_2 p_2 t}{N_S \mu_2}\right) \quad \ldots\ldots\ldots\ldots (2)$$

where by I is meant the inverse function of R.

To measure the contact potential across the film (V_{12}) as a function of the fraction of the surface (θ) covered it is therefore only necessary to measure V_{12} as a function of $p_2 t$. Experimentally this was effected by preparing the tube

with the oxygen at a known controlled pressure with the help of the barium dioxide filament, flashing the experimental filament at a high temperature to clean it and measuring the drift in the contact potential as the film reformed. A string galvanometer was used to take a record of V_{12} as the film formed. The pressure of oxygen was measured by means of an ionisation gauge, or for pressures exceeding 10^{-5} mms. of mercury by a Pirani gauge. The results from a series of experiments ranging from pressures of 7×10^{-8} to 10^{-4} mms. of

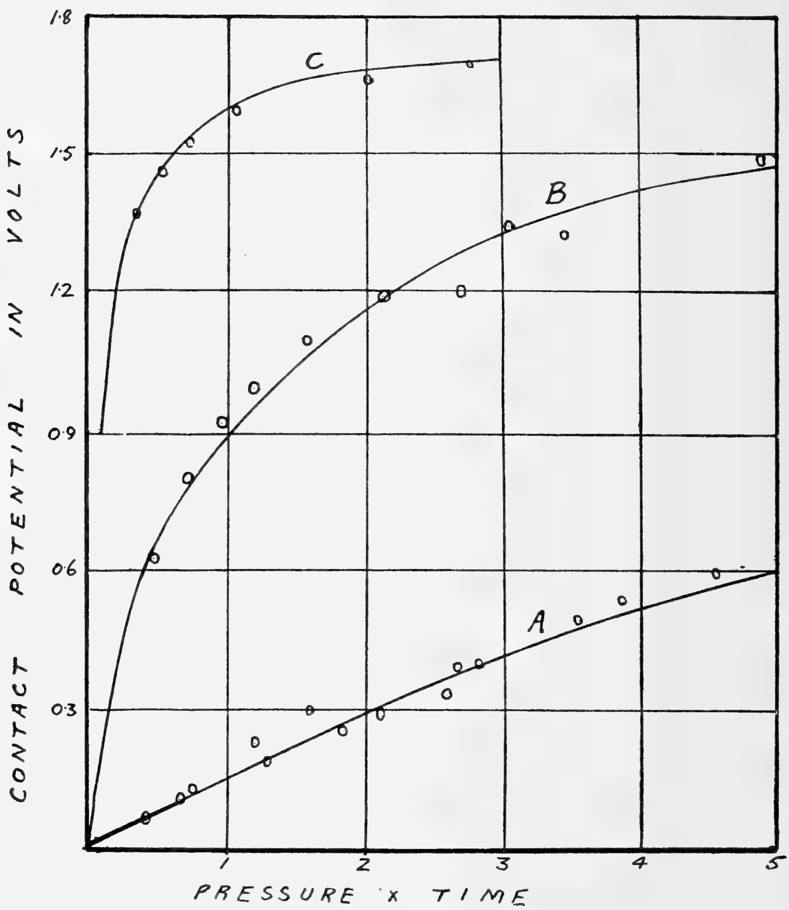

Figure 4.

mercury are recorded in Figure 4, in which p_2t is plotted against V_{12}. In curve A on this figure the p_2t scale is $2 \cdot 5 \times 10^{-7}$. The scale of curve B is ten times larger than this and the scale of curve C 100 times larger.

By using values of I calculated from the paper by Roberts, it is possible to calculate θ from p_2t provided α_2 is known. Since this factor is not known we can proceed further only by assuming some value for it and calculating the form for the resultant θ versus V_{12} curve. If for example θ is taken as unity, i.e. if we assume every molecule incident on to a bare surface sticks to that surface, then the θ, V_{12} curve must have a very pronounced inflection at about $\theta = 0 \cdot 5$. If on the other hand α_2 is assumed very small indeed (less than $0 \cdot 01$), the resultant θ, V_{12} curve has an equally pronounced inflection in the opposite direction.

Both these types of curve would be very difficult to interpret theoretically and we may safely regard as most probably accurate that particular value of α_2 which gives a θ versus V_{12} curve for which the inflection vanishes. The value of the condensation coefficient thus derived proves to be 0·40 and the resultant V_{12} versus θ has the form given in Figure 5. It will be observed that the curve is almost linear. Now the p.d. across the film (or V_{12}) is related to the dipole moment (μ) of the adsorbed atoms by the equation

$$V_{12}=1885\ \mu\sigma \text{ volts} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where σ is the number of adatoms per unit area of surface (or $1 \cdot 424 \times 10^{15}\theta$). We accordingly conclude that the dipole moment of the adatoms varies but little with the surface concentration. Table 2 gives some figures for μ calculated from Figure 5.

TABLE 2.
The Dipole Moment of Adsorbed Oxygen.

θ	0·0	0·2	0·4	0·6	0·8	1·0
μ in debyes ($=10^{-18}$ C.G.S. units) ..	−0·78	−0·76	−0·73	−0·71	−0·68	−0·66

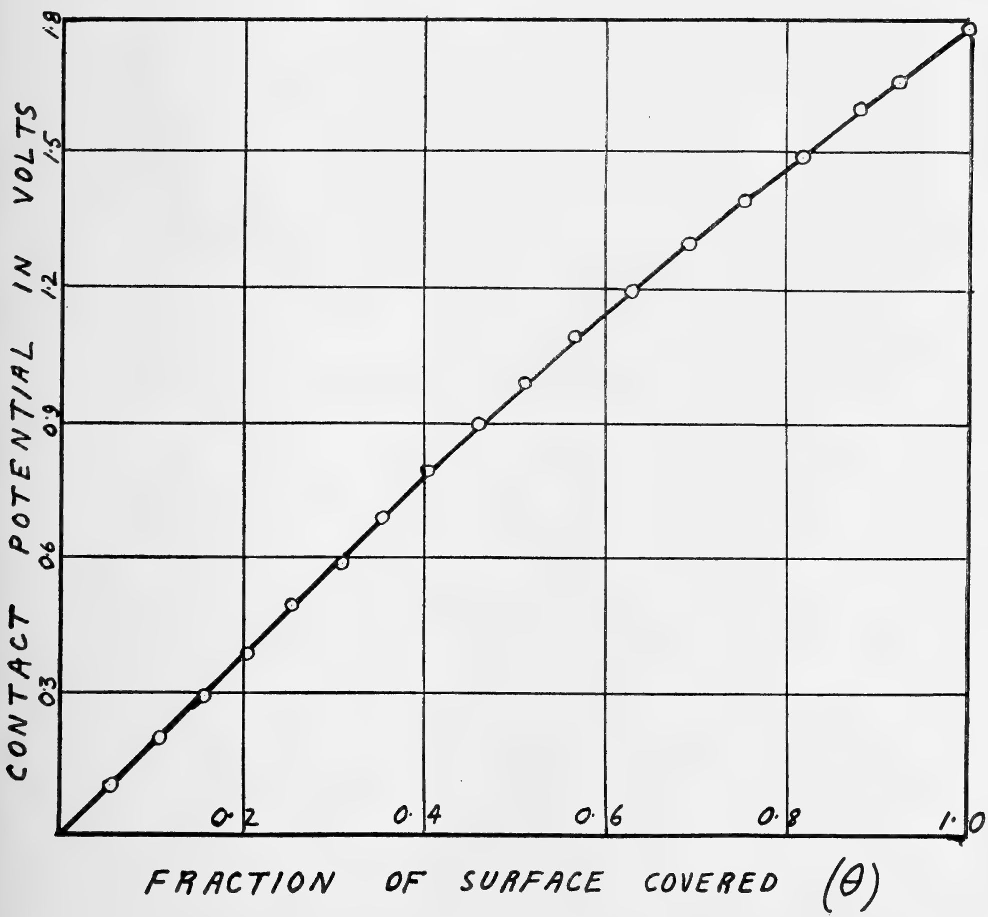

Figure 5.

Summary.

The contact potential difference method of measuring the work function of a surface may be regarded as an alternative to the thermionic method, in which however, the surface under study is maintained at a low and not at a high temperature. Whereas the thermionic method is available for the study of a few only of the more stable types of adsorbed films, the contact p.d. method in this field has a much wider range of usefulness.

The paper describes the apparatus for and mode of application of this method and shows how the method has been used in the study of the properties of electro-positive and of electro-negative films and in the measurement of vapour pressures. In the specific field of the condensation of oxygen on tungsten it is shown that the condensation coefficient is $0 \cdot 4$ and that the dipole moment of the adsorbed oxygen is practically independent of the surface concentration being $-0 \cdot 78$ debye units for a very dilute film and $-0 \cdot 66$ debye units for a monolayer.

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RADIANT HEAT LOSS AS A PROBLEM IN EFFUSION.

By R. C. L. Bosworth, M.Sc., D.Sc.(Adel.), Ph.D.(Cantab.), F.A.C.I., F.Inst.P.

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The loss of heat by radiation from heated and glowing gases can become more important than the loss by convection, particularly in large-scale equipment and at very high temperatures. Tables (McAdams, 1942) are available for the calculation of the emissivities of some of the better known gases such as CO_2, H_2O, SO_2 and certain hydrocarbons; at different temperatures, pressures and in equipment of different sizes, mainly as the result of the work of H. C. Hottel (1941) and co-workers. There does not appear, however, to be available in the cases of the less well-known gases any general method for the estimation of radiant heat losses in large-scale equipment from laboratory measurements. The object of the paper is to draw attention to the analogy which exists between high temperature radiative heat losses in gases at high or ordinary pressures and low pressure conductive heat losses in gases at low or ordinary temperatures.

A monochromatic beam of radiation of frequency ν passing a distance z through a gas at pressure p suffers absorption by a fractional amount

$$e^{-\alpha_\nu pz}$$

where α_ν is the absorption coefficient of the gas for this particular wavelength. Now the probability that a single molecule will travel a distance " z " through a gas is given by an analogous expression

$$e^{-z/\lambda_m}$$

where λ_m is the mean free path of the molecule concerned. We may thus regard the monochromatic radiation as consisting of photons or " fictitious " molecules of energy $h\nu$ each travelling with a velocity c along a mean free path λ_ν given by

$$\lambda_\nu=\frac{1}{\alpha p} \quad \dots\dots\dots\dots \quad (1)$$

In general, for radiation in a gas, λ_ν varies with the frequency (or energy of the photon), being low with a strong absorption band and practically infinite outside all absorption bands. λ_m for a gas molecule on the other hand is practically independent of the energy of the molecule. In addition, whereas λ_m at ordinary pressures is of the order 10^{-5} mms., λ_ν under the same conditions is usually of the order of meters.

Now in the gaseous conduction of heat across a phase boundary only those molecules within a distance of about one free path from the surface contribute heat to the surface, because only those molecules can get to the surface without making a prior collision. Consequently, the rate of interphase heat transfer is proportional to the surface area and to the temperature gradient at that surface. If, however, the mean free path is made greater than the thickness of the gaseous source, every molecule in it will contribute to the heat flow and the amount of heat crossing the boundary will be proportional to the volume and not to the surface area. There is an intermediate region with the mean free path of the same order as the dimensions of the source in which the heat loss is proportional jointly to the surface area and to the volume. In many problems of industrial heat transfer the mean free path of at least some of the photons concerned

is of the order of magnitude required for the intermediate region mentioned above.

In the instrument known as the Pirani gauge and used for the measurement of low pressure, the heat loss from a heated wire in an enclosed vessel with walls maintained at a constant temperature is measured (Pirani, 1906). Provided convection currents are eliminated, the heat loss from such a wire at ordinary pressures is independent both of the pressure and of the shape of the vessel. If, now, the pressure is reduced until the mean free path of the gaseous molecule is of the same order as the distance from the wire to the walls, the heat loss decreases with further decreasing pressure until when this has been so reduced that the mean free path is large in comparison with the dimensions of the vessel the heat loss due to conduction through the gas becomes directly proportional to the pressure and varies also with the size and shape of the vessel. If a series of different Pirani gauges geometrically similar but of different sizes were constructed, it could be shown that the heat loss due to gaseous conduction is the same function of pL for all vessels. The symbol p is used for the pressure and L for any characteristic linear dimension.

As a simple deduction for Beer's law, we may conclude that the high temperature loss of heat by radiation from glowing gases in geometrically similar vessels is also a function of pL, where now p is the partial pressure of the radiating gas and L any characteristic linear dimension of the vessels. The validity of this conclusion in view of possible deviations from Beer's law has been discussed by Becker (1925), von Bahr (1910) and Hottel and Egbert (1941). While some deviations are to be expected in the case of the more imperfect gases, it is generally concluded that the errors involved are slight.

We see, therefore, that both the low pressure conductive and high temperature radiative heat transfer in vessels of a given shape depend upon pL, and both for the same reason. The mean free path (λ) of the molecules or photons in the gas are (to a first approximation) inversely proportional to the pressure, and L/λ is a dimensionless quantity determining the probability that a given molecule (or photon) will suffer a collision before reaching the surface. Let us write, for the case of heat transfer by radiation of frequency ν,

$$p_\nu = A_\nu/\lambda_\nu \qquad \text{(2)}$$

and for heat transfer by conduction

$$p_m = A_m/\lambda_m \qquad \text{(3)}$$

where A_ν and A_m are the proportionality factors for radiative and conductive heat transfer respectively. If now we measure (*a*) the radiative heat loss r_∞ in units of heat per unit area per unit time for radiation of frequency ν in a vessel of dimensions so large or at a pressure so high that

$$\lambda_\nu << A_\nu p_\nu L\,;$$

(*b*) the radiative heat loss r_a of frequency ν under conditions

$$\lambda_\nu = aA_\nu p_\nu L$$

with a an arbitrary constant; (*c*) the conductive heat loss q_∞ in a geometrically similar vessel from a gas at such a pressure that

$$\lambda_m << A_m p_m L\,;$$

and finally (*d*) the conductive heat loss q_a in the same vessel but at a pressure $p_{m(a)}$, such that

$$\lambda_m = aA_m p_{m(a)} L$$

Then provided the same constant a applies both to the measurements of r_a and q_a, we may argue from analogy that

$$\frac{q_\infty}{q_a} = \frac{r_\infty}{r_a} \qquad \text{(4)}$$

Suppose, for example, that we had a glowing gas which exhibits in its infra-red absorption spectrum a single band of frequency ν_1 to ν_2, and that in this band the absorption coefficient α is constant. We require to know the emittance of the gas at a temperature T, partial pressure p, and contained in a long cylindrical vessel of diameter d. Were the gas layer thick enough to effect complete absorption within the band, the emittance could be obtained by drawing the radiant energy versus frequency curve for a black body at temperature T. The total area under this curve is, of course, σT^4, where σ is the Boltzmann constant. The area under the curve which lies within the absorption band from ν_1 to ν_2 is the quantity r_∞, while the emittance for a very thick gas layer is $r_\infty/\sigma T^4$. We require to know the quantity r_a (and the corresponding emissivity $r_a/\sigma T^4$) at a pressure p and diameter d. We set up a small scale model of the vessel in a thermostat and measure the conductive heat loss from a heated gas at such a pressure that the ratio

$$\frac{\text{Mean free path of the molecules in the model vessel}}{\text{Any characteristic dimension of the model}}$$

is the same as the ratio

$$\frac{\text{Mean free path of the photons in the prototype}}{\text{The corresponding linear dimension of the prototype}}$$

The heat loss thus measured is q_a. The quantity q_∞ may be obtained by raising the pressure in the model until no further increase in the conductive heat loss is experienced. The pressure, however, must not be raised so much that convection currents are set up.

Equation (4) may now be solved to give the required r_a, and thus the emittance. When, as is usually the case, the absorption spectrum effective at the temperature concerned contains a number of bands, bands of variable absorption coefficient, or both, it is necessary to split the spectrum up into a number of frequency steps over each of which an average constant value for α is assumed. For each such step we measure the contribution to the net r_a and sum all the individual contributions.

Example.

Mainly as a result of the work of Hottel and his collaborators, the emissivity of water vapour is comparatively well known. We will illustrate how the emissivity could be obtained from model experiments on thermal conduction. We require to know, say, the emissivity of H_2O at 2000° F. in a long cylindrical vessel of diameter one foot, the gas being present to the extent of 20% in a colourless diluent at atmospheric pressure.

pL is thus 0·2 foot-atmospheres.

The effective part of the infra-red absorption spectrum consists of three bands. The extent of the bands, for convenience of calculation taken as box-shaped, and their average absorption coefficient (in British Engineering Units), chosen to give the same average optical density as the actual diffuse bands, may be taken as

Band Number.	Wavelength Range.	Absorption Coefficient.
1	2·55–2·84 μ	3·25 ft.$^{-1}$ atmos.$^{-1}$
2	5·4 –7·6 μ	6·75 ,, ,,
3	12·0–25·0 μ	0·15 ,, ,,

L/λ for these three bands therefore amounts to

0·65, 1·35, 0·03.

A scale model of the cylindrical radiator, one centimetre in diameter, was set up and the heat lost from a central hot wire maintained at a fixed temperature

(*circa* 120° C.) above the temperature of the walls was measured, first at 10 mms. of mercury. The figure obtained (29·0 watts) was taken as q_∞. The pressure was then dropped to $6 \cdot 1 \times 10^{-3}$ mms. of mercury, at which pressure λ_m in air is 0·74 cm., so that $L/\lambda = 1 \cdot 35$. The heat loss, q_2, was 15·0 watts. Next the pressure was dropped to $2 \cdot 9 \times 10^{-3}$ mms., so that L/λ was 0·65. The heat lost, q_1, was measured as 9·5 watts. Finally, at $1 \cdot 35 \times 10^{-4}$ mms. where L/λ is 0·03, the heat lost, q_3, was 0·8 watts. We thus have

$$q_1/q_\infty = 0 \cdot 33$$
$$q_2/q_\infty = 0 \cdot 52$$
$$q_3/q_\infty = 0 \cdot 03$$

The curve for blackbody radiation at 2000° F. was then drawn and the area under each band estimated. These areas in relative measure are

Total area under curve	26·0
Area under Band 1	1·8
Area under Band 2	2·8
Area under Band 3	0·6

The required emissivity is therefore

$$\frac{1 \cdot 8 \times 0 \cdot 33 + 2 \cdot 8 \times 0 \cdot 52 + 0 \cdot 6 \times 0 \cdot 03}{26 \cdot 0}$$
$$= 0 \cdot 086.$$

The figure given in Perry's "Chemical Engineer's Handbook, 1941" for the emissivity of water vapour under the conditions above is 0·072.

While the method as illustrated by this example may appear rough in comparison with the standard method, it has the advantage of being available for all gases and vapours for which the infra-red absorption spectra are known, and for vessels of all shapes and sizes. It is necessary only to make the appropriate model in order to find what fraction of the energy in each absorption band contributes to the emissivity under the given conditions.

Since radiative heat transfer consists in the diffusion of photons of such a nature that the mean free path is usually of the same order as the linear dimensions of the vessel concerned, we may regard the problem as one of the effusion or "fictitious" molecules of energy $h\nu$, mass $\frac{h\nu}{c^2}$ and velocity c.

Summary.

A beam of radiation in a gas at pressure p and which exhibits an absorption coefficient α may be compared to a beam of molecules travelling with a mean free path $1/\alpha p$. Whereas, however, in normal problems of gaseous conduction the mean free path is much smaller than the linear dimensions of the vessel concerned, in problems of radiation the mean free path is often larger than the dimensions of the vessel. The flow of radiation in a gas is therefore akin to the low pressure effusion of gaseous molecules, and the paper introduces a method of calculating radiant heat losses from hot gases based on measurements carried out on low pressure gaseous conduction in small scale model vessels.

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SOME ASPECTS OF THE TECTONICS OF AUSTRALIA.

By E. S. Hills, D.Sc., Ph.D.*

Introduction.

One can, I think, pay no better tribute to the memory of our geological precursors than to analyse and synthesise the results of their labours, and to derive from them, to the extent that one's powers permit, a generalised impression of those great geological structures that are embraced in the scope of tectonics. In having been invited to deliver the Clarke Memorial Lecture for 1945, I appreciate the great honour that has been bestowed upon me, but having chosen to deal with some aspects of the tectonics of Australia, I feel also a keen sense of responsibility ; for to attempt to gather together, arrange and synthesise the writings of others, though aided by a slight acquaintanceship with some of the regions under discussion, does entail considerable mental hazards. I think, however, that the man whose memory we now keep green would have looked kindly on such an attempt. His interests were not restricted ; he devoted his attention with equal facility to gold mining or to details of palæontology, and in the resounding controversy into which he entered with Sir Frederick McCoy on the age of the coal measures of eastern Australia he showed his sound and balanced judgment, especially in his insistence on establishing geological relationships in the field. But that field work should be followed by laboratory and even by armchair study he would also have maintained, and it is increasingly borne upon me that geological science in Australia would have greatly benefited if the field geologists of official Surveys had been given more opportunities to carry out such studies than they have normally been afforded.

Part I. Pre-Cambrian Structures.

Introductory.

Since David published the first tectonic map of Australia in 1911, the problem of delineating the major elements in the structure of the continent has been attacked by several authors, each of whom has worked along rather different lines. David's maps (1911, 1932) show mainly generalised trend lines and folding directions ; Dr. Bryan (1932) has dealt with the early Palæozoic mobile belts and stable blocks ; Professor Cotton (1930) has interested himself more particularly in the pre-Cambrian, using the trend lines known at the time of his writing to outline certain pre-Cambrian massifs, and Mr. E. C. Andrews has represented on a series of maps the main elements of the Palæozoic structure of the continent (1937). In what follows, I shall attempt a more detailed analysis of pre-Cambrian structures, dealing for the most part with that relatively stable region which, for the moment, we may without further definition call the Australian Shield. This is a topic to which Mr. Andrews has already devoted some attention in his address on Some Major Problems in Structural Geology (1938).

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* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, June 13, 1945.

Warrawoona Structures.

In delineating the trend lines of pre-Cambrian rocks, one encounters so many difficulties that the attempt must be regarded as provisional with regard to details. Apart from the major difficulty of correlating pre-Cambrian formations in separate areas, one is strictly limited by the amount of detail recorded by the large numbers of workers upon whose arduous labours in the field our present interpretations are based. Professor de Courcey Clarke's work on Middle and West Australia (1938) affords the latest critical conspectus of pre-Cambrian formations, but it is convenient, following Professor Cotton's suggestion (1930), to adopt a threefold subdivision of the Western Australian pre-Cambrian succession for an Australia-wide nomenclature, since this procedure facilitates reference to David's map and to the numerous reports of the N.A.A.G.G.S. and of the Geological Survey of Western Australia. The accepted succession, which is here adopted, is as follows :

Nullagine System
(Unconformity).
Mosquito Creek System
(Unconformity).
Warrawoona System : Yilgarn Series—meta-sediments mainly.
Kalgoorlie Series—mainly meta-volcanic rocks (" greenstones ").
(Older rocks unknown in Western Australia. The Arunta Complex, Hutchison gneisses and Flinders granite of South Australia may be older (Clarke, 1938).)

In view of the uncertainty attaching to the correlation of isolated occurrences of pre-Cambrian rocks, I have included on the map of Warrawoona trends certain areas that have been classed as Mosquito Creek by others, e.g. the Kimberley Belt.[1] This includes altered basic lavas and tuffs, and lit-par-lit granitic gneisses, which indicate a Warrawoona age, in part at least, as advocated by Cotton (1930) and Clarke (1938). It may also be noted that the hematite quartzites and sedimentary iron ores that occur in this belt at Yampi Sound and Koolan Island are closely similar lithologically to the well-known " jaspilites " of the Western Australian goldfields, which occur in rocks of Warrawoona age. In places, these jaspilites make into large bodies of iron ore such as that at the Weld Range, and one may well question whether the accepted correlation of the Yampi Sound rocks with the Mosquito Creek system is well founded. Nevertheless, it seems clear that the sedimentary iron ores of the Middleback Ranges in South Australia are younger than the Hutchison Series of gneisses described by Tilley (1921), and David correlates them with the Mosquito Creek beds. On this view, there were in Australia two pre-Cambrian periods when sedimentary iron ores were deposited ; on the other hand, the Hutchison Series may be older than Warrawoona, as suggested by de Courcey Clarke (1938, p. 28), and all the important hematite-quartzite and sedimentary iron ore horizons of the pre-Cambrian (with the exception of the few Nullagine examples such as those in the Hamersley Range) may possibly, therefore, be Warrawoona in age. Such questions, although outside the scope of the present contribution, clearly affect considerations of tectonics, and I mention them as an indication that one's conclusions must be regarded as tentative until we have applied methods of correlation based on radio-activity to the pre-Cambrian rocks of Australia.

Other areas included on both the Warrawoona and Mosquito Creek maps are the Tanami and Tennant's Creek districts.

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[1] Regional names, in general, correspond with those used by Clarke (1938).

(i) Structure Elements.

The lines shown on the map are, so far as could be determined, a homogeneous group of structure elements, representing for the most part the trend either of foliation in gneisses and schists, or of fold axes, rather than the trend of outcrops. The stratigraphy and general structure of a very large area of the Western Australian goldfields have been admirably revealed during the long programme of detailed mapping carried out by the Western Australian Geological Survey, and it is now clear that in general the " Older Greenstones " are altered

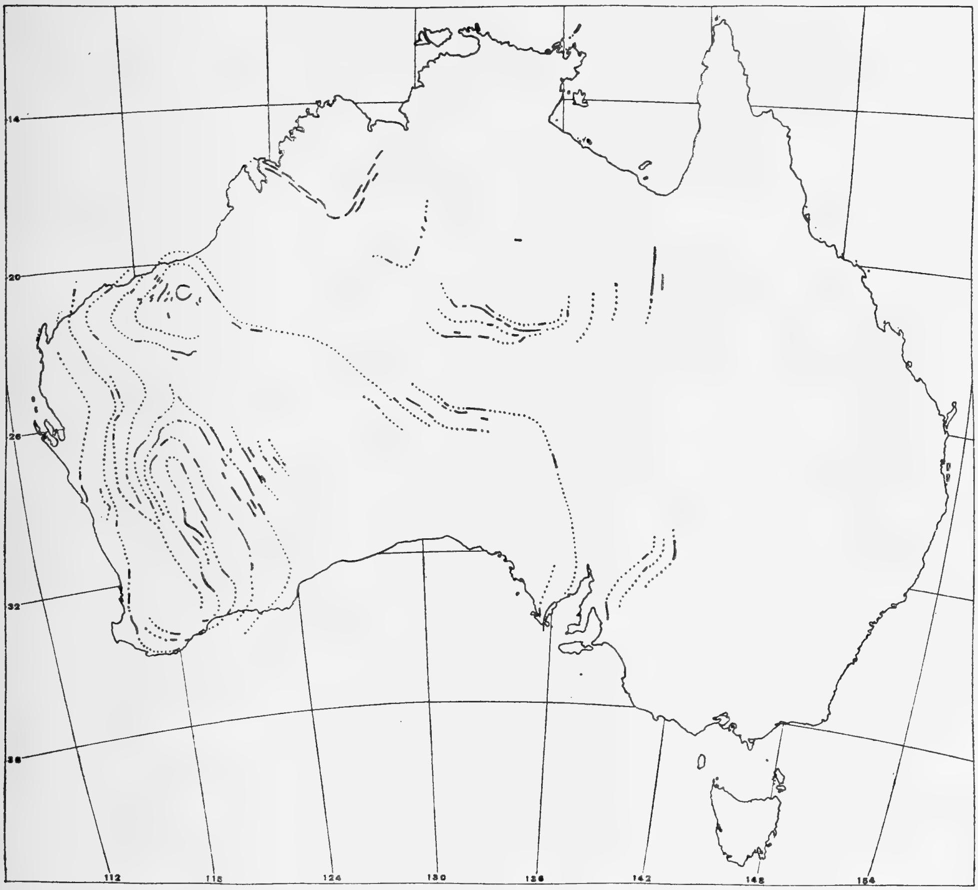

Fig. 1. " Warrawoona " (pre-Mosquito Creek) trend lines in Australia. Recorded strikes, heavy lines ; suggested extrapolations, dotted lines.

basic lavas and tuffs, as was first suggested by Honman. These rocks appear in the cores of major anticlines, flanked by younger conformable meta-sediments—the Whitestones of the Yilgarn Series.

Miles (1943) has demonstrated that in recording regional trends one must regard outcrops merely as a general guide, since, as in the Mt. Margaret area, the strata themselves may strike at right angles to the foliation and fold axes on the axes of pitching folds. Nevertheless, where outcrops trend uniformly for many miles, it is legitimate to regard them as delineating approximately the direction of fold axes, and it has been necessary to do this where mapping has not been completed in detail. The map (Fig. 1) includes all the reliable data as to trends of foliation and fold axes that I have been able to extract from the literature.

Inclination of Structure Elements. As a general rule, the Warrawoona rocks are strongly folded and the dip of foliation is vertical or nearly so. As Miles has pointed out, the foliation is mainly of the axial plane type, but in places the reports indicate foliation parallel to bedding as, for instance, in the area around Munglinup and the Young River, on the south coast. Here, as the strike of lithological units and foliation planes swings in a west to east traverse, from east-west to north-east and finally north-south, the dip of both ranges from 50°–90° S. to 30°–55° S.E. and finally to 40°–50° E. With dips as low as 30°–40°, unless the region is one of very strong overfolding, it would appear that the foliation is here not of the axial plane type.

(ii) Regional Notes.

I. Western Australia.

1. *Central Goldfields Region.* The general N.N.W. trend of fold axes and foliation in this region is well known, but marked deviation from this direction is found in the Cue-Meekatharra-Quinn's area, where the fold axes and foliation both swing sharply to the N.E. and even E.N.E. On the western flank of this structure the foliation returns again to N.N.W., but on the east, in the large greenstone " island " north-west of the Kimberley Range, sufficient structural details are not available to indicate the correct extrapolation of the N.E. striking rocks.

2. *South Coastal Region.* A remarkable deviation from the typical N.N.W. strikes occurs in the south coastal region of Western Australia. There are numerous records of strikes ranging from E.W. to N.E. in the area between the Porongorup Range and Hopetoun, and these have been confirmed for me by Professor E. de Courcey Clarke from his field notes. West of Hopetoun, however, the data are conflicting. Professor Clarke states that he has recorded as many N.-S. as E.-W. strikes in this district, and between Munglinup and the Young River the strikes swing in the N.E. quadrant. David (1932) ,however, indicates N.W. strikes about the Russell Range near the South Australian border, although the range itself strikes N.E.[2]

3. *Pilbara Goldfield.* The data available from the reports of the Geological Survey of Western Australia are here supplemented by the results of aerial and ground surveys of the N.A.A.G.G.S., giving a reasonably complete picture of a truly remarkable structure, with concentrically arranged trend-lines centred on an ovoid granitic intrusion east of Marble Bar. A detailed map of the area (Fig. 2) shows the circumferential arrangement which is outlined by the trends of strata, foliation and fold axes. The granitic intrusion, which is apparently not notably foliated except along its sheared margin, is 40 miles across in an E.-W. direction and 30 miles N.-S. If the concentric Warrawoona structures involved only schistosity, it might be possible to regard this as having been caused by the granitic intrusion, but it does not appear possible to attribute the trend of fold axes and formations to such a cause. Rather would it appear that the intrusion has followed a pre-existing, generally circular structure in the older rocks. Parallelism of granitic and pegmatitic masses with the trend of older rocks is, of course, a notable feature of the pre-Cambrian, but whatever may have been the origin of these granitic masses—be they the result of granitisation, of magmatic intrusion accompanying folding or following folding—the trend of formations in the country rock remains significant as an indication of the direction of diastrophic movements. I have, therefore, not concerned myself with the

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[2] Professor Clarke informs me that his statement (1938, p. 21), " Along and near the south coast, east of Long. 119°, the regional strike is roughly east and west " should have read " west of Long. 119° ".

effects of pre-Cambrian granitic intrusions on trend lines, since it appears to me that such effects were of a minor character.

Recorded trends in the Pilbara goldfield further removed from the Marble Bar district accord well with the conception that the concentric structure persists over a wide area, but one would wish to see further field work carried out in this region, which has interesting points of similarity with the Vredefort Dome and with large sub-circular concordant intrusions in California and Fenno-Scandia.

4. *Median Belt.* This belt lies mainly between the Pilbara goldfield and the Central goldfields and is defined by Professor de Courcey Clarke (1938) as extending from Lat. 26° to Lat. 22°. In the Median Belt, the general trend of

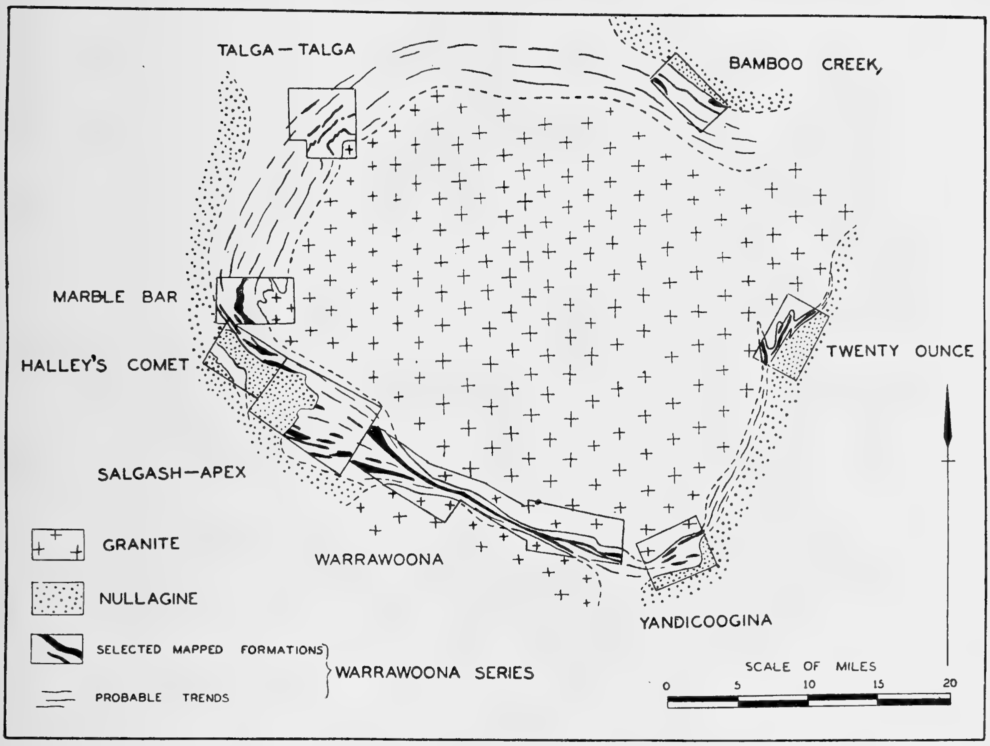

Fig. 2. Geological map of the district east of Marble Bar: base map after Gibb Maitland, details of mining centres after reports of the N.A.A.G.G.S.

all structures, excepting near the coast, is east-west, but unfortunately detailed observations have not been made in areas where the relationship of the E.-W. striking rocks to those with the more usual N.N.W. trend might be elucidated. Typical greenstones are rare in this region.

5. *Kimberley Belt.* As above noted, the strip of older pre-Cambrian rocks which outcrop around the margin of the Kimberley Plateau probably includes Warrawoona rocks. Interest centres in the V pattern, which as David has recorded (1911) is regarded by Gibb-Maitland as a "great syntactic arc". Hardman's mapping, however, shows that the western and eastern arms of the V are continuous in the south and the structure is therefore a deflection rather than a syntactic linkage of two distinct tectonic elements.

II. Central Australia.

The prevailing E.-W. strikes in the region have been recorded by many observers, but evidence is now available for limiting these trends on the east and west. Madigan (1937) has recorded N.-S. strikes in the gneisses near Mt. Playford, and in the country further east he found no evidence of a continuation of the Macdonnell Range structures. It seems that the influence of the meridional trends so markedly developed in the Argylla gneisses of the Cloncurry-Mt. Isa district is definitely indicated by these new reports. On the west, Hossfeld records persistent N.N.W. strikes in the Arunta Complex at Mt. Doreen, and northerly trends are also recorded between Tanami and Wave Hill by Jensen (1915), although the age of the rocks may perhaps be Mosquito Creek.

South of the Amadeus Trough, a swing to N.W. or N.N.W. at the western end of the belt of Archæan rocks in the Musgrave, Mann and Everard Ranges is also shown in the Warburton Range area.

Other areas where Warrawoona strikes are recorded call for no comment, but it may be noted that the Grey Range in south-western Queensland must now be removed from consideration, since the occurrence of ancient rocks there is not substantiated (Bryan, 1928).

In spite of the existence of gaps in the records of trends of Warrawoona rocks, it will, I think, be clear that some definite patterns can be made out. Alternative extrapolations to those given in Fig. 1 are possible, but whatever view one may take in particular instances, the general pattern resolves itself into strongly curved trends continuous over great distances, together with what appear to be concentrically arranged ring or ovoid units of very large dimensions. The concentric structure of the Pilbara goldfield, parts of the Central goldfields, the south coastal belt of Western Australia, and probably too of the Northern Territory, are, I think, fairly clear.

Some notably continuous trends are : (1) from the Mt. Lofty, Barossa and Flinders Ranges to the Everard and Mann Ranges, then to the southern edge of the Desert Basin in Western Australia ; (2) along the west coast of Western Australia, to link with line (1) on the north-west margin of the Pilbara goldfield. The significance of these structures will be referred to later.

Mosquito Creek Trends.

Rocks correlated with the Mosquito Creek System are of much more restricted occurrence than the Warrawoona.

1. *The Median Belt of Western Australia.* In this belt, Mosquito Creek beds occupy a number of isolated basins in which E.-W. strikes predominate, but the swing is from N.W. to S.W. (Fig. 3). In at least two areas it seems clear that the trend of the Mosquito Creek beds is widely divergent from that of the underlying Warrawoona rocks. These are the Uaroo district, where the trend of foliation in the Warrawoona gneisses ranges from N.N.W. to W.N.W., while the Mosquito Creek strikes are in general E.-W. : also the Eastern Creek area in Pilbara goldfield east of Nullagine (Finucane, 1939), where the Mosquito Creek beds again strike E.-W., and the Warrawoona generally N.N.W., but swinging. In this area, the N.A.A.G.G.S. claim to have established the existence of angular unconformities between the Warrawoona, Mosquito Creek and Nullagine rocks, respectively.

2. *Cloncurry-Mt. Isa-Lawn Hills Belt* (*Qld.*). Notable features in this district are the parallelism of trends in the Mosquito Creek (Mt. Isa) and Warrawoona (Argylla) series, and the well-marked deflection of the N.-S. trends characteristic of the Mt. Isa area, towards the N.E. at Lawn Hills ; further north, in the Border Area, the strikes are E.-W. or E.N.E. in rocks regarded by Jensen (1940*a*) as the equivalents of the Mt. Isa Series. The probable continuation of

this belt into the Northern Territory is seen in the MacArthur River sections described by Jensen (1914). There the dominant folding is on S.E.-trending axes.

3. *North Queensland.* Certain of the schistose and gneissic rocks in the Cape River, Einasleigh and Etheridge goldfields, and in Cape York Peninsula will be dealt with here although the age of the rocks is uncertain. That they are pre-Silurian appears clear from Ball's account of the Cardross area (1918) and

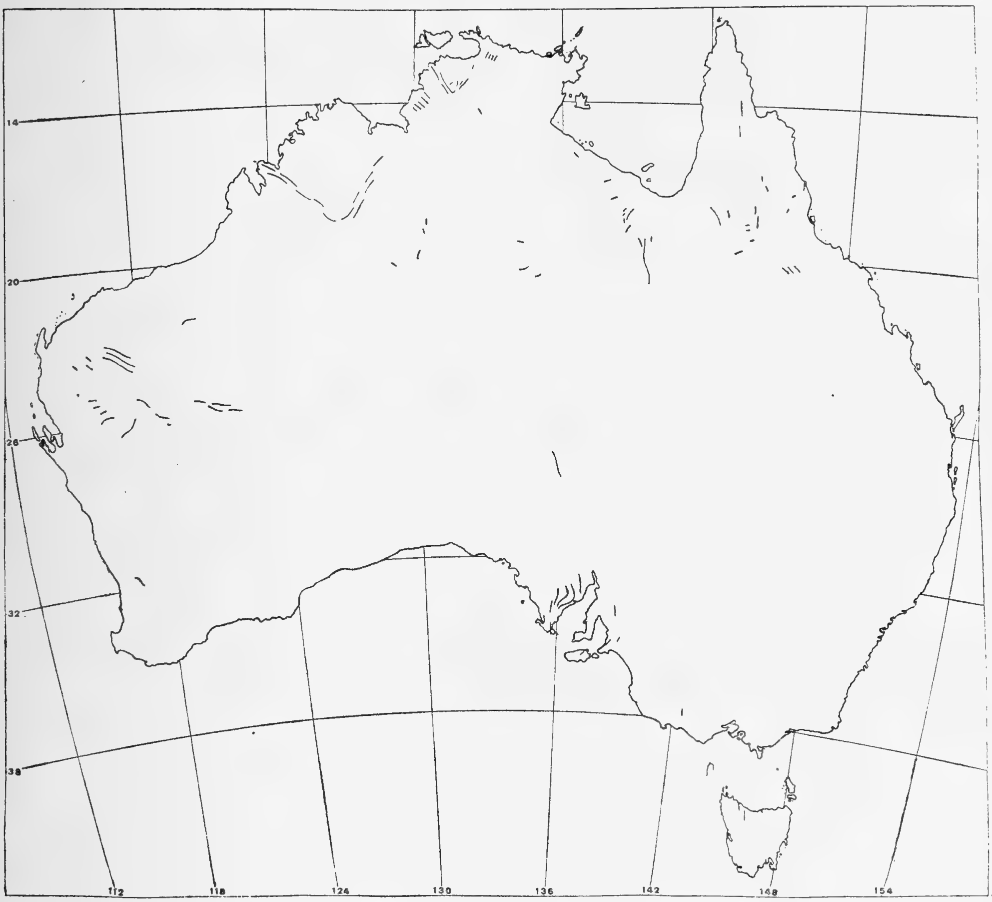

Fig. 3. Mosquito Creek trend lines in Australia.

from more recent work in the Palmer River goldfield (Jensen, 1940*b*). At the Portland Roads, iron ore deposits apparently similar to the hematite-quartzites of Yampi Sound and the Middleback Ranges occur, so that there is some justification for regarding the rocks in question as pre-Cambrian, in part at least.

It is maintained by Bryan (1925) that the gneisses of the Einasleigh and Copperfield Rivers (Einasleigh gneisses) are older than the schists, slates and lit-par-lit gneisses of the Etheridge, Gilbert and Woolgar areas (Etheridge Series), chiefly because of a right-angled discrepancy in strike between the two and the stronger metamorphic effects in the Einasleigh area, but it may be worth while to advance another point of view. Gregory (1884) and Jack (1887) both record N.-S. striking slates with granitic intrusions on the Etheridge River

near Crooked Creek, in the north-westerly continuation of the belt of E.-W. striking " Etheridgian " rocks, which in the intervening area are described by Gregory as being so disturbed as to have no definite strike. The maps of Cameron (1900) and Marks (1911) show that the Einasleigh and Etheridge districts were both invaded by the same foliated granitic mass and the direction of foliation is E.-W. in the Etheridge area (Cameron) and N.-S. in the Einasleigh area (Marks). Each series contains amphibolised diorite dykes, and thus there seems good reason for the field data to question whether the changing strike indicates a difference in age. It would, indeed, be quite legitimate to regard the Einasleigh gneisses as a strongly metamorphosed part of the Etheridge Series, and resulting in fact from post-Etheridge concordant intrusions.

The line along which the strike changes is occupied by the later porphyries of the Newcastle Range, which presumably were intruded along a line of weakness such as a sudden change in trend would provide. The map (Fig. 4) also indicates the possible structural relationship of the rocks above discussed to the folded felsites of Croydon, and to the schists of the Cape River goldfield, the Palmer River, the Hamilton and Coen goldfields, and the Cairns hinterland.

4. *Shatter Belt of South Australia.* In Eyre Peninsula, a similar right-angled change in strike from the N.-S. trends of the Middleback Ranges to E.-W. in the Cleve district also occurs. Further to the south, N.-S. strikes recur, so that the pattern is sigmoidal. Such rapid changes in strike are sufficient to show that extrapolation over any great distance is not justifiable in dealing with the older pre-Cambrian rocks of Australia.

5. *Pine Creek-Darwin Area.* The existence of a V pattern has long been known in the Pine Creek-Darwin area, having been recorded by David in 1911. The schists of the Buldiva-Collia and Fletcher's Gully areas remain parallel to the western arm of the V, and recent mapping has revealed the presence of a granitic intrusion apparently at the point of deflection near Brock's Creek. The structure lines in the country rock are concentrically arranged around the ovoid intrusion, thus affording an interesting comparison with the concentric structure near Marble Bar.

Nullagine Structures.

Excluding the Shatter Belt of South Australia and the Broken Hill district, Nullagine rocks are flat-lying or gently-dipping over very wide areas, and only locally they are either thrown into great monoclinal flexures or, more rarely, folded into anticlines and synclines. That the major structures of these rocks were formed in part during the Palæozoic era is clear where the Nullagines are followed without angular unconformity by the Cambrian as in the Ord River Valley and the Macdonnell Ranges. In these districts, as is well shown in the sections drawn by Wade (1924) and Madigan (1932), the Nullagine and conformably overlying Lower Palæozoic rocks partake of the same major structures. In Central Australia, the Ordovician Larapintine Series also conforms to the structures of the Nullagine and the Cambrian, and Mr. E. C. Andrews has suggested that the heavy conglomerates which form the upper part of the conformable succession in this region may be Silurian, and the age of the folding therefore Caledonian.

On the other hand, it is clear that the Amadeus Trough south of the Macdonnell Ranges was already outlined in Cambrian time, if not earlier, for the Ordovician sea transgressed on to the pre-Cambrian basement in the Mopunga Ranges (Tindale, 1931), also to the south of Cloncurry at Black Mountain (Whitehouse, 1936, p. 69) and probably also on the west in the Kintore Range near Lake Macdonald, where Cambrian limestones have not been recorded, and granite outcrops occur as a basement for (?) Ordovician sandstones (David,

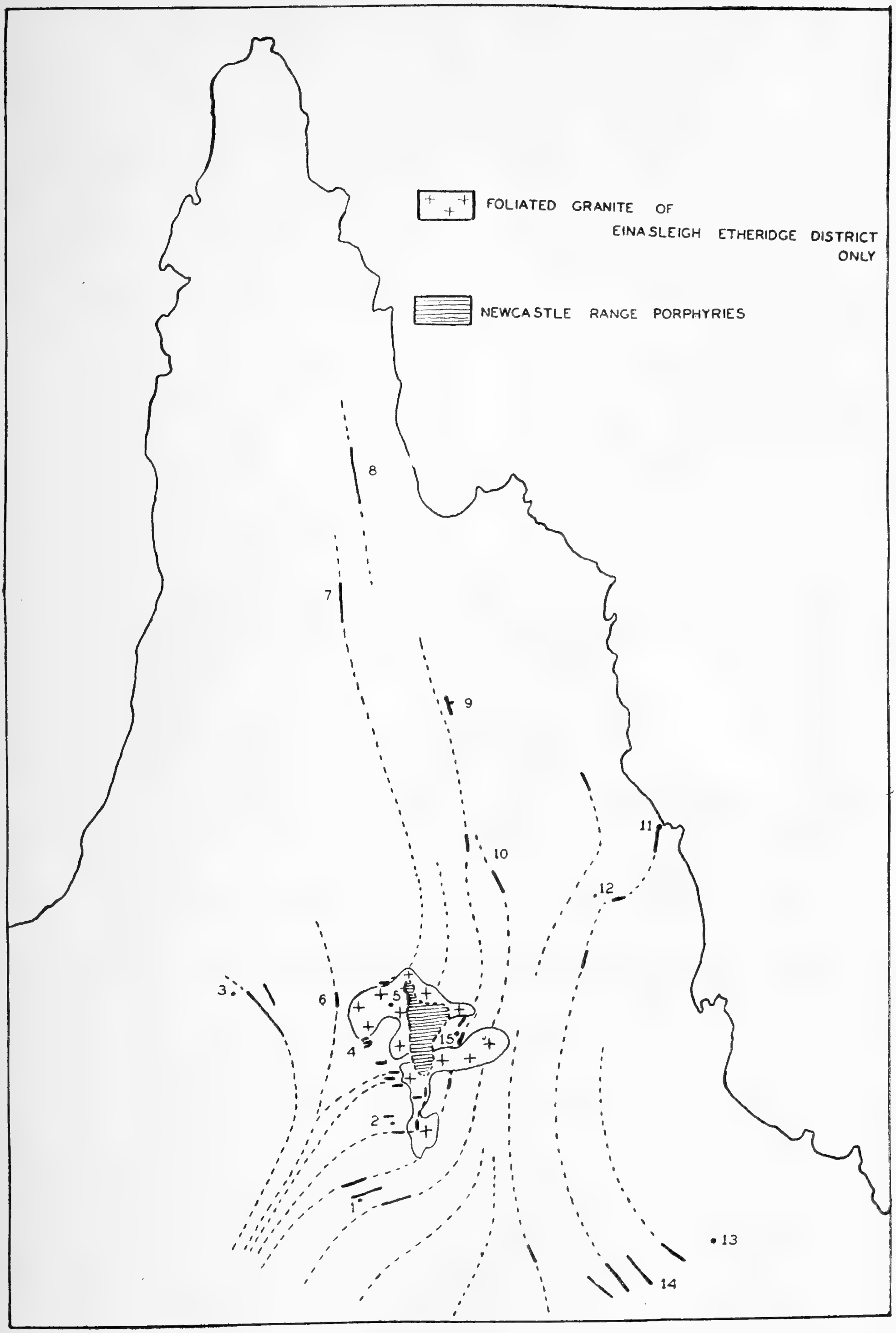

Fig. 4. Suggested trends of (?) pre-Cambrian rocks in North Queensland. Localities: 1, Woolgar; 2, Gilberton; 3, Croydon; 4, area of irregular strikes; 5, Georgetown; 6, Crooked Creek; 7, Musgrave; 8, Coen; 9, Palmer River; 10, Chillagoe; 11, Cairns; 12, Herberton district (pre-Devonian); 13, Charters Towers; 14, Cape River Goldfield.

1932). Similarly, the unfolded Cambrian rocks of the Barkly Tableland indicate the existence of a stable massif to the north of the persistent marine Amadeus Trough. It is, therefore, apparent that certain of the major structures exhibited by the Nullagine rocks were initiated at the very beginning of the Palæozoic era, and I will refer to the jointing, folding and tilting of these rocks as " Nullagine structures " in later remarks.

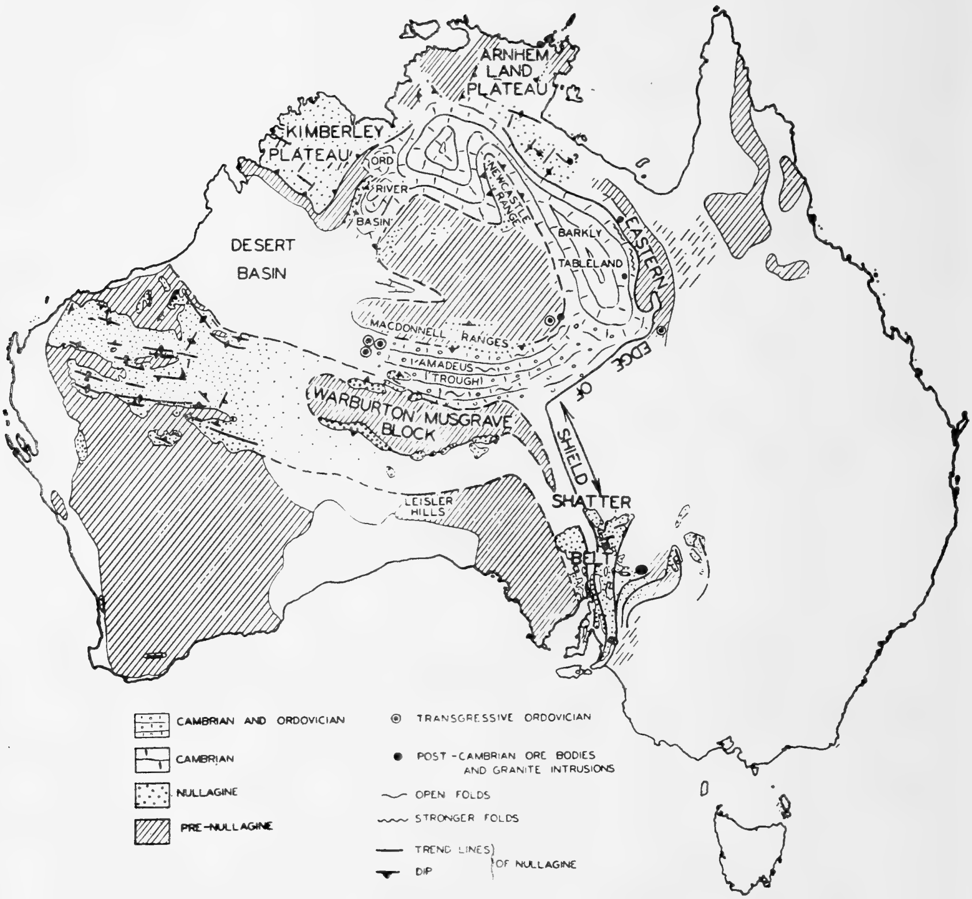

Fig. 5. Major elements of Nullagine-Cambro-Ordovician structure of the Australian Shield. Arrows indicate the suggested interconnection of the Amadeus Trough with the Shatter Belt.

In a broad view, one notes particularly the evidence, often repeated by various authors, that steep dips are of restricted occurrence and that over large areas the rocks are flat-lying. This applies even to Central Australia, where, although Voisey refers to " strong pressure " from north-south and east-west having acted on the Heavitree quartzite to produce thrust faulting, the same rocks are very little disturbed in the Mopunga and Hann Ranges further north. The Heavitree Range and its flanking Cambrian and Ordovician ridges, which extend in an almost straight line for over 250 miles from east to west, are, local complications apart, from the basset edges of a great flexure separating the Amadeus Trough from the dissected plateau to the north, as is well shown in Madigan's cross-section (1932). I suggest that this and similar structures

fundamentally involve differential vertical movements of large blocks rather than lateral compression. Local complications may, however, arise by compression in advance of the monoclinal flexure, as will be shown later, and these, it is suggested, may account for the folding and thrusting described by Voisey (1939).

Comparable Nullagine structures involving local flexing of otherwise flat-lying or gently-dipping strata, and resulting in places in vertical dips, are too numerous to be individually referred to, but they are well shown in Wade's sections of the Ord River basin (1924) and in Talbot's work on the North-west, Central and Eastern Divisions of Western Australia (1920). It is, moreover, worthy of note that these and other similar Nullagine structures persist laterally for great distances, and that many of the mountain ranges in areas of Nullagine rocks have, like the Macdonnell Ranges, resulted from differential erosion. This applies to the Albert Edward Range east of Hall's Creek, which may be followed northwards to the Dixon Range for a distance of over 100 miles. The King Leopold Ranges on the south-western margin of the Kimberley Plateau are of similar structure and extend for a similar distance; so also is the escarpment on the western edge of the plateau of Arnhem Land.

Indeed, excluding the Shatter Belt of South Australia and the Broken Hill district, it may be recognised as a general rule that the Nullagine rocks, considered broadly, exhibit a truly magnificent series of vast upwarped and downwarped blocks. The structural type is in some ways comparable with the Saxonian fault-folding—*Bruchfaltung*—but is developed over an incomparably greater area.

Major Elements of Nullagine Structure.

Considering for the moment only these major elements of Nullagine structure, we may recognise certain tectonic units shown in Fig. 5. Notice the plateau regions within which the Nullagine and later rocks are flat-lying or greatly inclined, as in the Kimberley Plateau and the Barkly Tableland; also the relatively depressed troughs such as the Ord River Basin, and the upthrown blocks in which older pre-Cambrian rocks are exposed.

The Plateau of Arnhem Land, although covered superficially by a veneer of Mesozoic (? Cretaceous) sedimentary rocks, is essentially composed of Nullagine and (?) Cambrian formations. On the grand western escarpments the Nullagine conglomerates and quartzites dip easterly, and it is probable that the Mitchell and Parsons Ranges on the east are of similar structure with westerly-dipping rocks.

In the Barkly Tableland, too, the flat-lying Cambrian limestones and sandstones are underlain for the most part by Nullagine quartzites which appear around the margin of the Cambrian area.

South of the Amadeus Trough, the distribution and dip of quartzites that unconformably overlie the older pre-Cambrian rocks, as synthesised on David's Geological Map of Australia, permit one to recognise that the Mann, Everard, Musgrave and associated Ranges are relics of a raised block, flanked to the north and south by Nullagine quartzites which dip off the elevated region. In the core of the block, the older rocks are exposed, and their reappearance in the Leisler Hills, and in a wide area north of Eyre Peninsula, indicates that we have, to the south, another raised block which is probably continuous with the Central and Southern goldfields of Western Australia. This latter region is flanked on the west at the Darling Scarp by remnants of younger sedimentary formations now referred to the Nullagine (Clarke, 1938), and in the Stirling Ranges, too, the presence of (?) Nullagine rocks indicates the proximity of the margin of the upwarped area.

In the Northern Territory, between Tennant's Creek and Newcastle Waters, Nullagine rocks appear from beneath the Cambrian limestones of the Barkly Tableland. They strike N.N.W. in the low Newcastle Range, but near Attack Creek in the south there is a remarkably sudden swing to the E.-W. trend characteristic of the Macdonnell Range belt. To the north-west of the Newcastle Range, underground water of similar type to that of the Barkly Tableland is obtained from bores on the Murranji stock route ; limestone of Cambrian type occurs in many places as, for example, north of Tanami (Jensen, 1915), and its

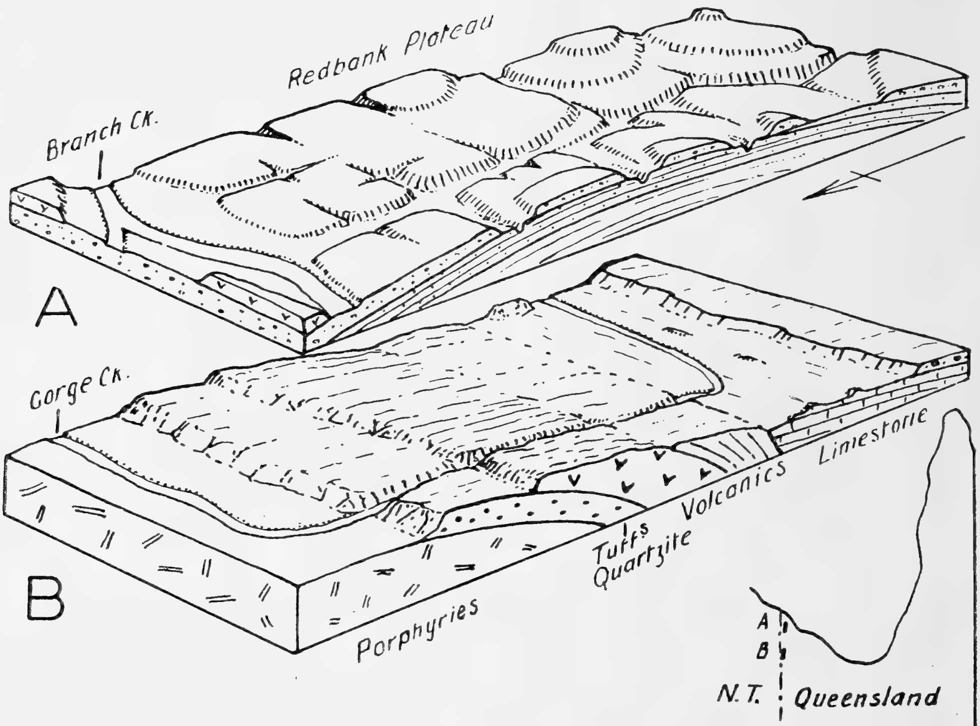

Fig. 6.

A. Pattern drainage controlled by major jointing in the Redbank Plateau. Length of section, about $1\frac{1}{2}$ miles.

B. Cambrian (?) limestone faulted against pre-Cambrian rocks north of Nicholson River. Length of section, 3 miles.

presence in depth in the depression south of The Granites is suspected from the occurrence of travertine at the surface (Hossfeld, 1940). It is, therefore, probable that the area of Cambrian rocks in the Territory is larger than appears on existing maps, and that the blocks intervening between the Cambrian areas, and in which Nullagine and older rocks are exposed as shown in Fig. 5, are relatively upwarped. The suggested outlines of the blocks shown are, however, purely diagrammatic in this region since the geology is so little known.

Pattern of Folding, Faulting and Jointing.

A glance at the maps (Figs. 5, 8) on which the details of recorded Nullagine structures are shown is sufficient to indicate that in any one region the trends of flexures, folds and major joints follow two dominant directions, approximately

at right angles to each other. The influence of major joints in determining the rectangular drainage pattern of the southern Kimberley Plateau has already been pointed out by Jutson (1934), and on the Northern Territory-Queensland border the Redbank Plateau affords another excellent example (Fig. 7 (A)). There can be no doubt as to the conjugate nature of these two directions, and therefore the folding, flexing and tilting of the Nullagine rocks along similar conjugate directions, as is well exemplified in the Kimberley area and Median Belt of Western Australia, calls for some explanation. Since each fold is itself a simple structure (Fig. 7 (B)), it is not possible to attribute the cross folding and flexing to later

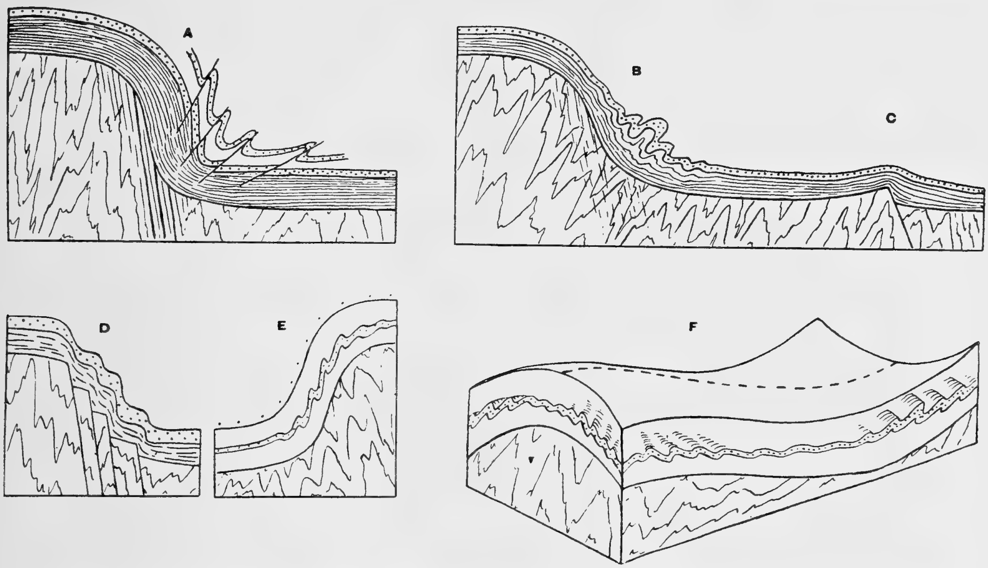

Fig. 7. Suggested origin of minor folds and faults in Nullagine and Cambrian strata overlying a crystalline basement-complex.

(A) Reverse faults in core of monocline.

(B) Folds in core of monocline.

(C), (D) Folding induced by faulting in the basement.

(E) Drag folding in a monocline.

(F) Transverse drag-folds in centroclinal folds.

diastrophism affecting strata already folded on one trend line ; thus the folds and flexures, although trending at right-angles to each other, must be regarded as synchronous.

I cannot, myself, envisage any mechanism whereby such structures could result from regional compression, but they could readily have been caused by differential vertical movements among a mosaic of blocks of rectangular outline, and we have already seen that differential vertical movements of blocks affords an adequate explanation of the larger Nullagine structural elements. Faulting in the basement, for example, may be transmitted to the overburden so as to form folds of the Plains type, and faulting combined with tilting of basement blocks produces similar though more marked effects (Fig. 7 (C)).

On the other hand, there are strongly folded zones in the Nullagine of Western Australia, as in the Ethel Gorge north of the Opthalmia Range, and in the Bangemall district, which require some other explanation, and the thrust and drag-fold phenomena on the southern flanks of the Eastern Macdonnell Ranges described by Voisey (1939) also call for comment. Such features, which are in

every case limited to definite zones associated in the field with great monoclinal flexures, may, I suggest, have resulted mainly from local compression developed in the concavities of the flexures, as discussed by Willis (1935). Various possible effects are shown in Fig. 7, and it will be seen that, according to the physical properties of the involved strata, the local compression may be expressed either as thrust faulting or as folding. In addition to the effects of squeezing, drag folding of thinly laminated or more plastic rocks such as limestone or dolomite

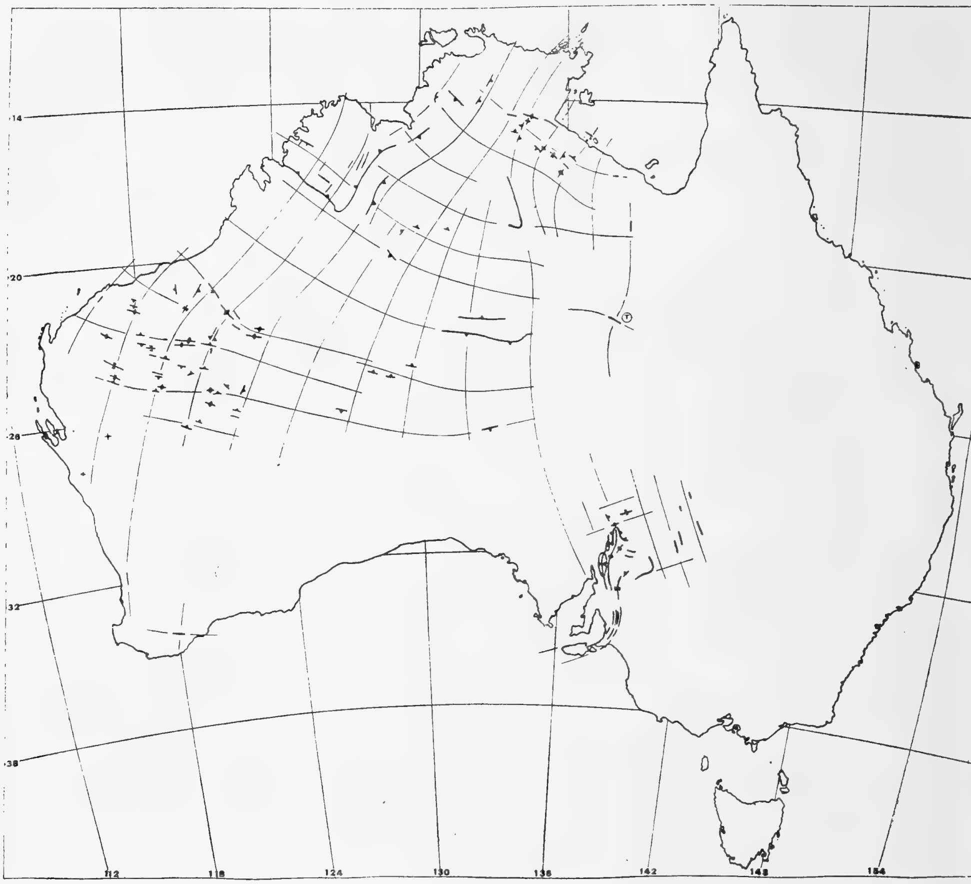

Fig. 8. The Nullagine structural pattern. Observed trends, thick lines ; projected trends, thin lines. T, Toko Range fault (Nullagine not exposed).

lying between massive competent beds may account for some of the observed folds. Such disharmonic folding has already been described in the eastern Macdonnell Ranges by Voisey and in the Flinders Ranges by Howchin (1922).

The Flinders-Barossa-Mt. Lofty belt of South Australia has up to now been excluded from discussion. The Nullagine and lower Palæozoic rocks are strongly folded in the southern part of this belt, as shown by Hossfeld (1935), but in the north they exhibit a most unusual combination of great domes and basins, as shown by Mawson (1942) and termed by him " Pound Structure ". The axis of elongation of the domes and basins corresponds to the trend of fold axes further south, but in the North Flinders Ranges near Mt. Painter (Mawson, 1923) and at the Sliding Rock Copper Mine (Dickinson, 1944), close folds trend at right-angles to the major axis. Nevertheless, the dominant northerly trend also

persists, as in the ranges flanking the Leigh Creek basin on the west. It seems likely, therefore, that the cross folds recorded are drag-folds. At the Sliding Rock mine, they occur in weak Cambrian limestone, and the cross folding may have resulted from the unusual direction of bedding-plane-slip brought about during the formation of the centroclinal " pound " type of structure (Fig. 7 (F)).

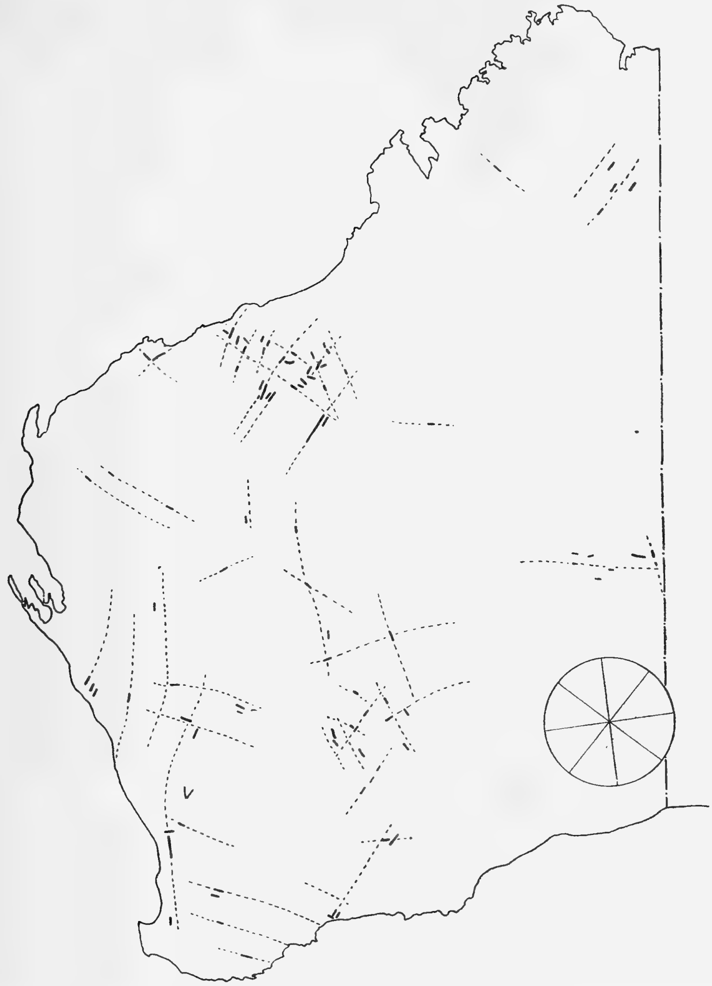

Fig. 9. Tentative map of dykes in Western Australia—exclusive of concordant acidic intrusions. Dykes, heavy lines; suggested extrapolations, broken lines.

The Nullagine Fracture Pattern.

On the map showing Nullagine trends (Fig. 5), it is clear that there is a regional swing in the two dominant directions, and that as one trend gradually changes, the conjugate set changes in sympathy. Such a gradual deflection is shown, for instance, along the southern margin of the Desert Basin in Western Australia. I have, therefore, attempted to synthesise the pattern of Nullagine structures on the assumption that such gradual changes in trend occur, and the resultant pattern, which, if the arguments put forward above are correct, is a fracture-pattern, is shown in Fig. 8. It is, I think, worthy of note that over the

vast area represented, the method of drawing two conjugate directions which, in general, swing only gradually, does indeed accord with the pattern of recorded structures without violent disharmony in any area.

The net of Nullagine structures seems so regular that one would have little hesitation in using it as a basis for extrapolation into areas of unknown structure. Such prognostication is, in fact, one of the most valuable practical applications of tectonic analysis, and one that must in future be more widely used as an important adjunct in both geological reconnaissance and the more detailed investigations connected with the search for economic mineral deposits.

A rectangular fracture pattern of this type may have resulted from shearing in a horizontal plane, from torsion, or from regional up and down warping. Hans Cloos (1939) has shown experimentally that in an upwarped area tension gashes are arranged at 90° to each other, and that the trends gradually change on the margins of the upwarp. With regional doming or basining, the crust is subjected to a more or less uniform extension, resulting in tension centrifugally directed from the centre of the warped area. That such tension could be expressed both as normal faulting and by the opening of tension gashes, up which dykes might make their way, seems a reasonable assumption. I, therefore, suggest that this pattern very probably resulted from regional warping, and it may even be that the great median geosynclinal trough which crosses the continent is to be compared with those *Graben* that transect broadly upwarped regions, and which are genetically related to the regional tension developed in the crustal arch.

Dyke Rocks of Western Australia.

An interesting comparison may be made, although only tentatively, between the Nullagine structural net and the pattern of dyke rocks in Western Australia. The map (Fig. 9) includes dykes of various geological relationships, but the lit-par-lit granitic and pegmatitic intrusions have been excluded from consideration. Study of the literature alone admittedly does not form an adequate basis for an investigation of this type, but in spite of such inaccuracies of interpretation as have unavoidably been made, it does appear that there are possibly represented two fracture patterns, each consisting of conjugate directions at right angles. Comparison with Fig. 8 indicates that one of these sets follows the Nullagine pattern fairly closely, while the other is developed at about 45° to it. This may indicate that dykes of two or more distinct ages are represented, but there is also a possibility that subsidiary fractures at 45° to the dominant lines may have developed in connection with the Nullagine pattern itself.

Part II. Interpretation and Discussion.

1. *The Significance of Warrawoona Tectonics.*

(*a*) *Pantectogenesis.* A notable feature of the Warrawoona system throughout Australia is its apparently ubiquitous strong folding and regional metamorphism. R. T. Chamberlin (1924) has remarked that in areas where the older pre-Cambrian rocks are now exposed they have for the most part been subject to several periods of orogenic deformation, but over a vast area of Australia, the latest important deformation by compression and folding considerably antedated the Nullagine period; even if my interpretation of Nullagine structures in terms of differential vertical movements is not agreed to, the fact still remains that these rocks are so little disturbed over great areas that the structures of the underlying rocks can have been but little modified by post Proterozoic deformation.

As we have seen, too, the main trend of the Warrawoona rocks was probably not greatly changed by the post-Mosquito Creek folding, for east-west trending

Mosquito Creek beds repose on N.N.W. trending Warrawoona rocks in the area where the latter trend is characteristic for the older rocks, and elsewhere the trends of the two series are essentially parallel, with no indication that the older structures were deformed into conformity with the younger.

Considering now the vast Central goldfields area of Western Australia, about one-quarter million square miles in extent, we see that it exhibits a notable homogeneity of structure and lithology, and when it is realised that the present location of the greenstone belts was determined largely by folding, the remarkable nature of this folding becomes evident. It was of such a type that the greenstones of the Kalgoorlie Series were repeatedly brought to the same general level in the crust, so that outcrops of the greenstones continually recur across the strike, over a distance of at least 400 miles. The folding, therefore, was, in contradistinction to that characteristic of Palæozoic and later time, of a regional nature, and was not restricted into definite zones. With such a clear example to guide us, we may speculate more widely concerning the area west of Long. 142°, including most of South Australia, the Northern Territory and Western Australia, and assume that the tectonic pattern shown in Fig. 1 is for the most part homogeneous and was determined largely, although not entirely, by the post-Yilgarn revolution. It then appears that we do indeed have to deal with a tectonic phenomenon of a most unusual type. One can recognise both long folded zones and regions of concentric folding, all probably formed during the one major episode, and adjoining each other so that a vast area was folded. Mountain chains, if formed at all, must have been subsidiary in folding of this type, and the process cannot therefore be referred to as "orogeny". Major structural features were, however, developed, and I suggest that the process should be regarded as part of the general process of "tectogenesis", or the formation of major tectonic elements. In view of its widespread effects, I propose to designate it "pan-tectogenesis", and "orogenesis" may in this terminology be regarded as a type of tectogenesis restricted to definite zones of mountain-making. Ruedemann (1920-21, 1923) in his studies of the pre-Cambrian trends of the continents has already suggested that Archæozoic folding was nearly universal, and although his ideas have been criticised by Miller (1923), it does appear even in a global view that such ancient folding was much less restricted into orogenic zones than was that of later times.

Pan-tectogenesis of the type one may recognise in Australia involved folding about centres or tectonic foci. The resultant pattern suggests that a kind of skimming process may have gone on whereby the crustal rocks of the time were crumpled, thickened, and aggregated together into compact units, which may well represent the primitive continental nuclei of Australia. In Fig. 10 the nuclei that appear to be represented in Australia are shown.

There is, in addition, evidence, especially on the western margin of the present continent, that the aggregated units were finally surrounded by an enclosing belt of folds, the trends of which sweep smoothly around groups of nuclei.

As to the mechanism by which such tectonic elements may have been formed, it seems obvious that one cannot apply the usual conception of stable or rigid masses moving together to compress intervening soft sediments with a vice-like action. It is necessary, I think, to postulate forces that could act over very great areas, and which also could be directed towards the tectonic foci. Convection currents in the substratum would appear to afford the most likely motive agent. Griggs (1939) has shown that the drag of convection currents on the base of the crust should be adequate to cause crustal buckling even with conditions as they are today, and it seems likely that the structure of the earth's outer shells during the early pre-Cambrian would have been more favourable to such deformation, since the sialic layer was presumably thinner at that time.

With convection in the substratum, centralised folding could result either from upward or downward currents emanating from or directed towards columns in which the flow was vertical. Encompassing groups of smaller centres, there might also have been larger currents which would have produced the more persistent marginal trends and perhaps would have caused the smaller units to move together, and subsequently have held them united as a group. Above

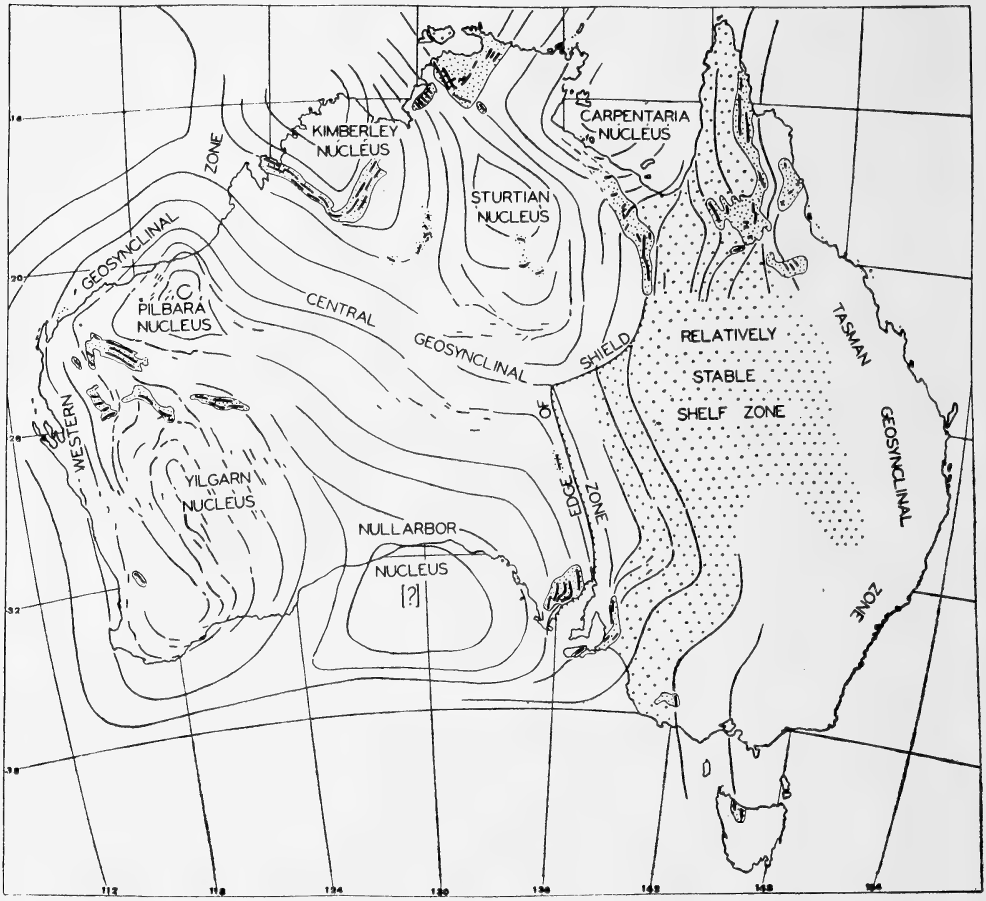

Fig. 10. Tectonic map of Australia, showing suggested older pre-Cambrian trends (generalized); Mosquito Creek rocks, close stipple; shelf zone, open stipple.

centrifugal convection centres the crust would naturally be thinned, and above centripetal centres it would be thickened. Thus the major massifs resulting should represent centripetal areas, and traces of the centrifugal centres would probably be lost during any subsequent drawing together of the individual massifs. Thus, it may be speculated, the original continental mass of Australia perhaps originated.

Major Tectonic Elements of Australia.

In analysing the tectonics of Australia, one's attention should not rigidly be restricted to the existing continent. Dr. Bryan has recently discussed in the Clarke Memorial Lecture for 1944 the question of the former easterly extension

of Australia, and I wish merely to add a few remarks on matters that arise from our present considerations. For those geologists who accept the conception of Gondwanaland as a vast landmass linking the southern continents and Peninsular India, and including also the area now occupied by the Indian Ocean, Australia is but a fragment of a former vast continental mass. Ruedemann (1920-21) found that this conception agreed with his world-wide study of pre-Cambrian trends, but his generalisation of Australian trend lines as meridional over the whole continent is unacceptable.

Returning to the ideas set out above concerning the evolution of continental masses in pre-Cambrian times, we have seen that ancient trend lines and structures in Australia indicate a primary aggregation of the older pre-Cambrian crust into a large unit by the gathering together of smaller elementary nuclei, and it is suggested that the primitive continent was rounded off by a continuous series of circumferential folds. As to how far those structures which are now preserved on the west coast of Australia formerly extended to the west we have little to guide us, but there is nothing to suggest that they extended far. An indication of the limits of the continent may perhaps be afforded by the distribution of Cainozoic volcanic rocks. The tectonic phenomena in the west are not strictly comparable with those in the east of Australia, but the occurrence of Cainozoic volcanic activity over an area of 3,000 square miles in the south-west of Western Australia, also in the Fitzroy Valley where the post-Permian leucitite plugs described by Wade and Prider are most probably Cainozoic, may be considered as analogous with the phenomena in the eastern Cordillera, thus giving an indication that the true edge of the continent is not a vast distance removed. The Permian and Mesozoic geosynclinal deposits laid down on the western fringe of the continent afford a further indication that an important tectonic break follows this line fairly closely.

The Australian Shield.

In the subdivision of the Australian continent itself on a tectonic basis, we may note first of all that there is clear evidence, with which you will already be familiar, for the existence of blocks that have been relatively stable over long periods, and of zones marked by greater or lesser degrees of mobility. The existence of mobile belts on the earth from Karelian times onward is now a commonplace in geological teaching, but there is little agreement as to the fundamental factors that influence the stability or mobility of various parts of the crust.

The relative mobility of eastern Australia as compared with the area west of about Long. 142° E. is too well known to call for comment, and in this contribution I have so far dealt mainly with the more stable region which has been termed the Australian Shield.

The eastern mobile belt is distinguishable from the shield area not only by the record of sedimentation, but also by the occurrence in the complex geosynclinal zone of Palæozoic and later volcanic rocks, of granitic intrusions and associated ore deposits, and of strong folding of Cambrian and later Palæozoic and even Mesozoic rocks. The regional distribution of these geological phenomena may, therefore, be used to define the limits of the shield and of the mobile zone.

The most westerly known occurrences of strongly folded Nullagine and Cambrian rocks, of post-Cambrian granitic intrusions, and of post-Cambrian ore deposits presumably of magmatic origin are shown in Fig. 5. They indicate that the eastern edge of the Shield extends from the Shatter Belt of South Australia to the Lawn Hills district in Western Queensland. Further continuation is uncertain, but very probably the line turns north-west to the MacArthur River, where some of the folded limestones may be Cambrian, and the tectonic

conditions are compared by Jensen (1940) with those at Redbank, at which locality some post-Nullagine mineralisation apparently occurs.

Madigan's reference (1937) to post-Cambrian unstressed granites in the Dulcie Range indicates the importance of the major structural line which delimits the southern edge of the Barkly Tableland. This line, north of which undeformed Cambrian rocks occur on the Tableland, trends W.N.W. from the Toko Range, where the Ordovician is faulted against the Cambrian (Whitehouse, 1940) and probably marks the northern edge of the marine trough which during those periods allowed the sea to enter central Australia from the south (Fig. 5).

Immediately to the east of the edge of the Shield as here defined, the older rocks are for the most part hidden beneath Mesozoic and Tertiary sediments of the Great Artesian Basin and the Murray Basin. In Queensland, schistose rocks are met with on the floor of the Artesian Basin, but the age of these is unknown. Rocks regarded as pre-Cambrian occur as we have seen in north Queensland, and in tectonic contact with these old rocks at Chillagoe, Mungana and the Palmer River, there are strongly sheared Silurian sediments. It thus appears that in the complex Tasman geosynclinal zone of eastern Australia, a pre-Cambrian basement occurs and that this basement was broken down when the geosyncline was initiated. How far the basement extended eastwards into and beyond the Tasman Sea, Dr. Bryan has already discussed with you.

That it is possible to further subdivide both the Shield and the mobile belt into subsidiary massifs and troughs has already been demonstrated by Cotton, Bryan, Andrews and Tindale. I do not desire to enter on a critical discussion of the details of the tectonic subdivisions already proposed, for there is sufficient common ground in all for our present purposes. It may be noted, however, that a broad zone adjoining the Shield on the east possesses much greater stability than the Tasman Geosyncline itself. This zone has been the site of marine incursions mainly of shallow transgressive type, probably during the Palæozoic and certainly during the Mesozoic and Tertiary, and may be likened to a shelf or rim bordering the Shield, although separated from it by a belt of weakness. For the most part, this shelf zone corresponds with the eastern massif recognised by Dr. Bryan (1932).

It will be seen by comparing Figs. 5 and 10 that the main subdivision of the Shield is afforded by the long and persistent central geosynclinal trough that extended from the Shatter Belt through the Amadeus Trough to the Desert Basin during parts of Palæozoic time. This trough itself is outlined by a long sweeping line of Warrawoona trends. In the south, the trough follows the edge of the Shield as above defined, but in central Australia it abruptly departs from this line, as if the Shield had yielded along cross-fractures.

Along the coast of Western Australia, the Permian and Mesozoic geosynclines (Andrews, 1937 ; Teichert, 1939) likewise follow with almost exact conformity the sweeping Warrawoona trend lines.

On the other hand, the stable nuclei correspond to areas of central folding in the Warrawoona rocks. It is the intervening and circumferential zones that have the greater mobility. This relationship may be connected with the suggested origin of the structures—the nuclei representing areas of thickening of the sialic crust and the intervening and circumferential zones being thinner and thus weaker. We begin then to see, as would indeed be expected, that the tectonic elements in the Australian Shield have a structural basis. Let us now trace the influence of the structure-lines a little further.

The Nullagine Fracture Pattern.

We have already seen that the Nullagine rocks exhibit a pattern of intersecting and complementary fractures, but in addition there is revealed with the greatest clarity in practically all parts of the Shield, either an almost exact

parallelism of Nullagine and older trends, or an almost right-angled relationship between them. This fact has been referred to by many workers, but is singled out for special comment by Talbot (1920). A notable example is afforded along

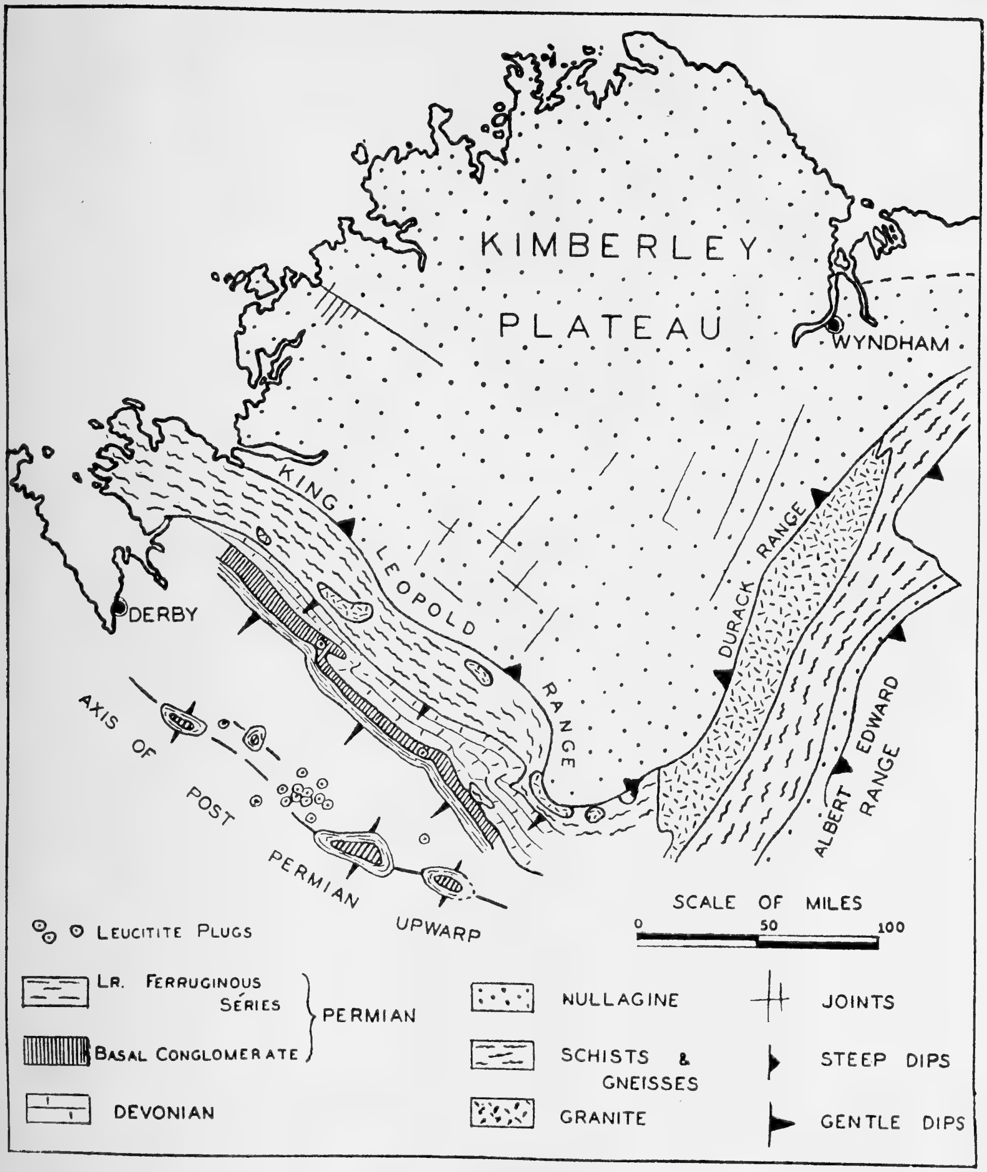

Fig. 11. Geological map of the Kimberley district, Western Australia, after David, Wade and Prider, and Hardmann, with emendations.

the margin of the Kimberley Plateau, where on the south-west the Nullagine rocks of the King Leopold Ranges trend parallel to the foliation of the underlying gneisses and schists, and on the east the Durack Range and the Albert Edward Range bear a similar relationship to the older rocks, although the strike in this district is so different from that on the west.

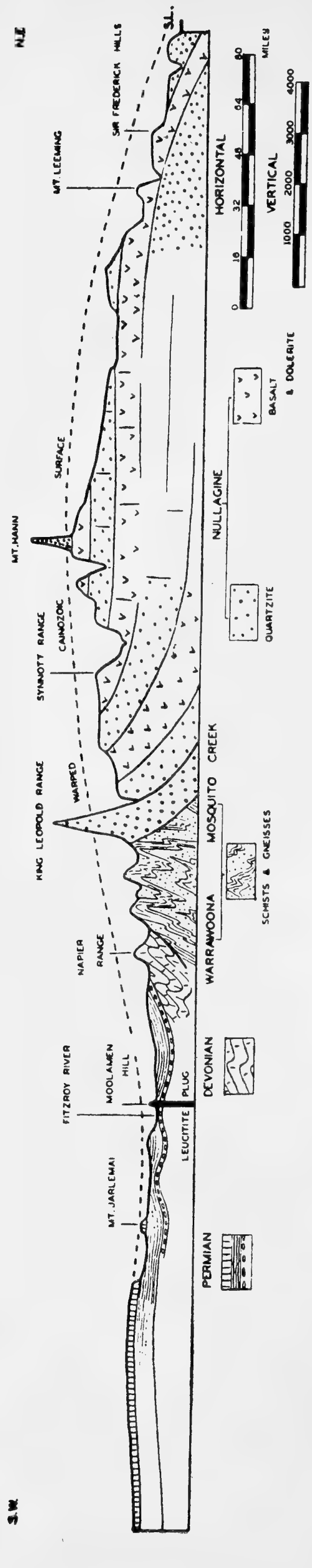

Fig. 12. Sketch section across the Kimberley district.

Many other examples, including the Macdonnell Ranges over their whole length of more than 250 miles, will be obvious by comparison of Figs. 1 and 8.

In view of this relationship, the significance of the swing in the Nullagine fracture pattern becomes clearer. The swinging trend was determined not entirely by the orientation of the stress axes in an isotropic medium, but largely by predetermined structural lines in the continent, which yielded preferentially under stress. The tendency to form conjugate fractures in the first instance was clearly the result of the stress, but the precise direction of yielding was determined by the anisotropy of the basement rocks. The existence of such control by old structures is, I think, a tectonic principle of the greatest importance, especially in dealing with relatively stable regions.

Consequent Tectonics.

It is unnecessary to stress the fact that the Tertiary faulting in the Shatter Belt followed almost exactly the pre-Cambrian and Cambrian structural lines, as may be seen by reference to Fenner's maps (1930). Again, in the Kimberley area, the strike of the Devonian sedimentary formations and also of the Permian which unconformably overlie them, is parallel to the trends in the older pre-Cambrian basement and to the Nullagine of the King Leopold Ranges. Furthermore, the numerous leucitite plugs described by Wade and Prider (1940) are clearly aligned on the same trend, which has also been followed by the axis of post-Cretaceous warping. The old trends therefore clearly reflected in the present topography (Figs. 11-13). These relationships indicate that undulatory movements have affected the area from pre-Cambrian to Tertiary times along the persistent trends of the Warrawoona rocks, at times allowing marine incursions to take place, and at other times causing the sea to retreat and the rocks to be folded along the old N.W.-trending structure lines. Notice may also be taken of the trend of the Permian and Mesozoic geosyncline that borders the Australian Shield on the west. The curves of this trough conform almost exactly to the pre-Cambrian strikes; so also the outward bulge of the continental mass, revealed by submarine contours, parallels the curvature of the N.W. quadrant of the concentric structure of the Pilbara goldfield. Other examples of similar relationships could readily be adduced, but I will not labour the point.

Recognition of the exercise of control by older structures over younger is nothing new in geology, but it is to Ruedemann that we owe the clearest statement of the influence of pre-Cambrian trends, especially in North America, in determining the fundamental grain in the continents. Schwinner (1936) has also

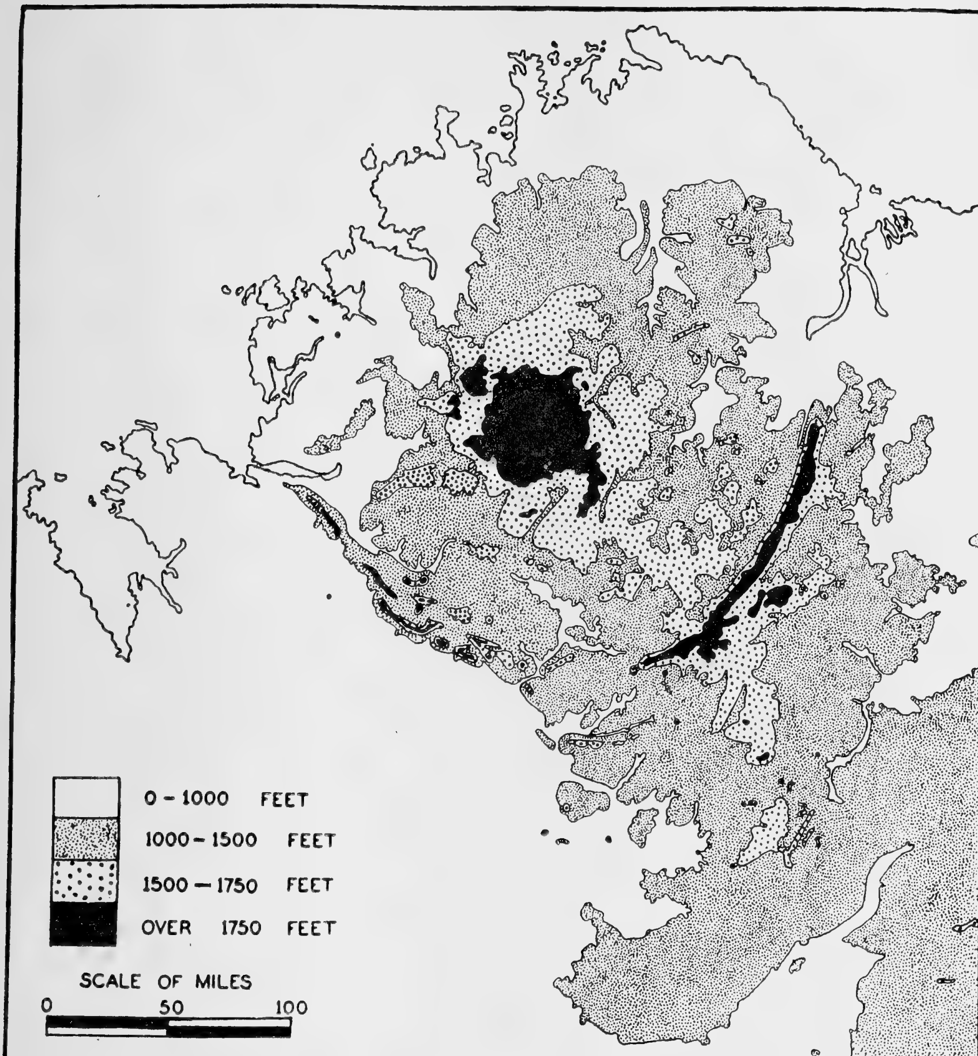

Fig. 13. Topographic map of the Kimberley district, based on a model prepared in the Geology Department, University of Melbourne.

shown that in Europe the tectonics of Palæozoic and later rocks are related to a pattern of pre-Cambrian structures, and he has used the term "consequent tectonics" to express this relationship.

In view of the various data that have been presented, it will, I think, be clear that the mobile and stable regions of Australia differ in their structure and strength. A mobile belt is such, not because it has been subjected to greater stress than other regions, but because it is fundamentally weaker than the stable nuclei or massifs.

In recognising the existence of stable nuclei and relatively mobile zones in the Australian Shield, I have reached, though by a different route, similar conclusions to Bryan, Cotton and Andrews. Andrews regards the old nuclei as having been welded together by the compression of Palæozoic geosynclines; I would suggest, however, that the welding took place much earlier, although leaving zones of weakness between the nuclei and around the margins of the continent, and that the structure as a whole is perhaps but little more stable now than it was when it was first formed. For instance, the initiation of quite deep Tertiary troughs in the Shatter Belt of South Australia indicates continuing relative mobility of the old Nullagine-Cambro-Ordovician trough. Perhaps if the diastrophic forces acting on the continent were increased, the old zone of weakness even in the interior would once again become an important marine trough.

That the main mass of Australia was already continental, and that the Shield area possessed considerable stability even before the Nullagine period may, I think, be gathered from the probable distribution and lithology of the Nullagine rocks. Their present distribution has been greatly affected by subsequent earth movements and erosion, but the occurrence of the various scattered remnants, such as those now recognised along the Darling Scarp and in the Stirling Ranges in Western Australia, is such as to strongly suggest that the Nullagines were originally laid down over practically the whole of the Shield and as far east as Broken Hill. They were laid down on a peneplained surface of older rocks, and their typically arenaceous and rudaceous lithology indicate uniformity in the conditions of sedimentation over their wide areas. There is, therefore, I suggest, no necessity to think in terms of welding the nuclei together after the Nullagine period for that welding had apparently taken place long before; subsequent geological events have, rather, revealed the flaws in the primitive continental mass. The main zones of weakness have repeatedly manifested themselves up to Cainozoic times, and the grain formed in the early pre-Cambrian has continued to influence later structures to such a degree that one may well wonder to what extent the great mobile belts of the earth, despite their youthful exuberance, may themselves have been subject to similar parental control.

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PART III

FRICTION BETWEEN KERATIN SURFACES AS AFFECTED BY SOME SHRINKPROOFING TREATMENTS.

By M. Lipson, B.Sc., A.A.C.I.,
and P. Howard, B.Sc.

Manuscript received, July 11, 1945. Read, August 1, 1945.

Introduction.

Wool and other animal fibres show a greater frictional resistance when rubbed from tip to base than from base to tip. Monge (1790) appears to have been the first to record this fact, attributing it to an overlapping scale structure in the fibres, which was used to explain the felting properties of wool. This explanation of felting, based on unidirectional migration of fibres due to their physical surface properties or scaliness, has greatly dominated the ideas of subsequent workers. Recently, however, Martin (1944) has put forward the view that the difference in frictional properties is not so much due to the physical structure of the scales as to their surface chemical composition. In support of this he quotes the lack of correlation between microscopic appearance of the scales and actual frictional measurements and also the presence of a directional frictional effect in forms of keratin without scales such as finger nails and polished porcupine quills. In addition there is the fact that certain wools which have been made non-felting still possess a scale structure, but little or no directional frictional effect.

For the actual determination of the surface frictional properties of wool fibres, several methods have been used. Speakman and Stott (1931) described an apparatus for examining the frictional properties of one wool surface against another which made use of the inclined plane technique. Fifty fibres were mounted on a small wooden bow with their scales all pointing in the same direction. The measurements of friction were carried out using an inclined plane, the surface of which was covered with a trail pile finished wool cloth. The method was later adapted by Speakman, Stott and Chang (1933) to determine frictional properties in water. Whewell, Rigelhaupt and Selim (1944) applied the inclined plane method to demonstrate that treatment of wool with certain of the commercial non-felting reagents brought about a reduction in the directional friction effect. When wool was treated with a $0 \cdot 2$ N solution of chlorine in carbon tetrachloride they showed that although the directional frictional effect was reduced, the actual values for the angles of friction increase. A full report of their experiments had not come to hand at the time of writing the present paper.

Bohm (1945) has also reported the results of experiments using groups of fibres in the form of a uniform sheet of several hundred and sliding them against a glass surface.

Chamberlain and Speakman (1942) described another method applicable to individual fibres which depends upon the tension developed by the migrating fibre as it is mechanically rubbed between two moving surfaces. This method was used by Barr and Speakman (1944) to adduce evidence in support of their theory that unshrinkability produced by treatment with mercuric acetate or benzoquinone was not due to a reduction in scaliness in the treated wools.

What is probably the most accurate method is that devised by Mercer (1945), who used a modification of the stick-slip apparatus of Bowden and Leben (1939) to examine the frictional properties of individual fibres. By using this apparatus, he showed that the directional frictional effect is reduced when wool is treated with commercial unshrinkable processes. In general his results are in agreement with those of Whewell *et al.* (1944) but differ in one respect. The latter workers record a decreased directional coefficient but *increases* in actual frictional values when wool is treated with chlorine, whereas Mercer shows that the decrease in directional coefficient is due to substantial *decreases* in actual frictional values. Although Whewell *et al.* used a solution of chlorine in carbon tetrachloride in their experiments, whilst Mercer used an aqueous solution of chlorine, the differences in their results are such as to warrant further investigation. Furthermore, both workers have confined their measurements to the friction shown by treated wool fibres against surfaces which have not been treated by the unshrinkable reagents. This procedure is not strictly correct, as in studying the effect of non-felting reagents we are concerned with the friction of treated fibres against each other. For this reason, the present investigations have included experiments in which frictional measurements have been made using treated fibres sliding on treated surfaces of keratin.

We first experimented with the inclined plane technique, but it soon was apparent that the time and patience required to fix the fibres on the sliding bow would not permit the carrying out of large numbers of measurements. As the equipment used in other methods was not readily available, a technique was devised using comparatively simple apparatus which was briefly described in an earlier paper (Lipson, 1945). It is proposed now to give a fuller description of the method, together with results of investigations on some of the problems outlined above.

Description of Apparatus.

The set up is shown in Plate IV, and as can be seen from this, no unusual equipment is needed. The main requirement is a small cylindrical rod of keratin of approximately 8 mm. diameter. The rods used in the present experiments were turned from cattle horn. Two hooks each weighing 0·1 gm. are attached by means of molten shellac to either end of the fibre, which is then suspended over the rod. The solution in which the frictional determinations are required siphons from the conical flask on to the bulb of the thermometer and then drops on the fibre rod junction. The contents of the flask are heated until the thermometer above the rod records whatever experimental temperature is required. All the measurements described in this paper were carried out in a solution containing 0·2% soap and 0·1 sodium carbonate at 35° C., the pH value being 10·7. The bent glass rod placed in contact with the underside of the cylinder carries away the solution after use. During measurements the tap on the siphon is regulated so that the solution drops rapidly on to the fibre-rod junction.

To carry out a frictional determination, weights consisting of calibrated pieces of wire are gradually added to one of the hooks until the fibre commences to slide in that direction. As the initial movement of the fibre is extremely slow, it is desirable to use a magnifying eyepiece during observations. For simplicity this has been omitted from the photograph. An observation is made one minute after the addition of each weight, and if no movement is shown another weight is added. The experiment is then repeated, adding weights to the other hook and again carefully observing the commencement of sliding. The measurements are made to the nearest 0·01 gm. The hooks are next removed and each is weighed, together with attached shellac. The total load in direction of motion (W1) is the sum of added weights and the weight of hook plus shellac. The coefficient of friction in each direction is calculated from the

formula for a sliding rope around a post. If W2 is the weight of hook plus shellac on the other end of the fibre, then $\frac{W1}{W2}=e\mu\theta$, where μ=coefficient of friction in direction of motion and θ=angle subtended by normals from directions of W1 and W2.

As W1 and W2 are both vertical, then $\theta=180°=\pi$ radians, and the expression can be simplified to $\mu=0{\cdot}736 \log_{10} \frac{W1}{W2}$

From this formula the coefficients of friction in either direction can be calculated. The above formula is applicable only if there is uniform contact between fibre and rod. That this is so is demonstrated by the gradual movement of the fibre when sliding occurs, which is usually of the order of 0·5 cm. per minute and often less.

Experimental.

The wool used was prepared from a 64's quality merino fleece of good length, uniformity and freedom from excessive dirt and vegetable material. The fleece was purified by extraction with boiling petroleum ether (boiling range 50–80° C.) to remove the wax, followed by extraction with warm distilled water to remove the suint. The small amount of residual dirt was allowed to fall out on opening the clean dry staples.

The keratin rods were prepared from the tips of cattle horns which had been turned on a lathe to cylinders of diameter 8 mm. Departures from this diameter were found to have no serious influence upon the experimental results. It is desirable to have the surface of the keratin rod smooth but not highly polished. In this way high values for the coefficient of friction are obtained and the order of accuracy of the method is thereby increased. Each horn sample before use was washed with ether, alcohol and distilled water.

Table 1 shows the results of frictional measurements using the same fibre but with different samples of horn. It can be seen that there is good agreement between the figures obtained.

Table 1.

Frictional Measurements of One Fibre on Different Samples of Horn.

Fibre.	Horn.	μ1.*	μ2.*	D.F.E.*
No. 10	Sample A	0·35	0·11	0·52
,,	,, B	0·30	0·13	0·40
,,	,, C	0·31	0·13	0·41

* In all tables μ1=anti-scale coefficient, μ2=with-scale coefficient, Directional frictional effect (D.F.E.)=$\frac{\mu 1-\mu 2}{\mu 1+\mu 2}$.

The unshrinkable treatments adopted throughout the work were as follows:

Sulphuryl Chloride. Treatment in a 2·5% by volume solution in carbon tetrachloride for one hour at 18–19° C. followed by washing with carbon tetrachloride, rinsing in water, neutralising in 0·1% sodium carbonate solution and finally washing thoroughly in water.

Alcoholic Caustic Potash. Treatment was carried out with a 2% solution in 95% alcohol for 18 minutes at 26° C. This was followed by washing in 95% alcohol, neutralising in 1% by volume alcoholic sulphuric acid, washing in water, and finally treating with 0·1% sodium carbonate solution and washing thoroughly in water.

Aqueous Bromine. The fibres being examined were made up in weight to 1 gm. by the addition of more wool, the fibres under test being kept separate by attaching them to glass rods.

Treatment was with 6% of the wool weight of bromine in a volume of 200 ml. of water. Treatment was for one hour at 19° C. at the end of which the wool was washed in water and placed into 1% sodium bisulphite solution. This was followed by washing in water, treatment with 0·5% sodium bicarbonate and again washing with water.

Aqueous Chlorine. The conditions were as for aqueous bromine, the chlorine solution for treating 1 gm. of wool being prepared by adding 50 ml. of deci-normal hydrochloric acid to the requisite amount of 4% sodium hypochlorite solution and making up to 200 ml. with water.

Chlorine in Carbon Tetrachloride. Treatment was with 0·2 N chlorine in carbon tetrachloride using 1 gm. wool in 20 ml. reagent and proceeding as with wet bromine. The wool was washed with carbon tetrachloride after chlorination and before treatment with sodium bisulphite.

In those experiments in which the cylinders of horn were tested, the conditions of treatment were the same as for wool.

Effects of Unshrinkable Treatments.

The first series of experiments was designed to observe the effect when the horn and not the fibre was treated by the unshrinkable reagents. This was carried out by determining the friction of three separate fibres against a horn sample and then treating the latter with one of the unshrinkable reagents and repeating the frictional measurements. The effects of five of the unshrinkable processes on five different samples of horn were thereby observed, using five different groups of fibres.

The results have been recorded in Table 2, and it can be clearly seen that treatment of the horn samples with the various reagents has in all instances significantly lowered the apparent directional coefficients of all the fibres. Sulphuryl chloride, bromine and chlorine have all reduced the anti-scale coefficients of friction to below one-quarter of their original values. With alcoholic caustic potash the reduction is to about one-half of the original values. The with-scale coefficients of friction have also been significantly reduced in treating with sulphuryl chloride and the halogens, but not with alcoholic potash. The figures for directional frictional effect should be accepted with reserve, as when we are concerned with coefficients of friction approaching zero, small variations cause marked differences in the directional frictional effect. This is evident in fibres No. 24 and No. 25 in the experiments using aqueous chlorine. The former has a directional frictional effect of 0·33, whereas that of the latter is zero. Yet it is doubtful whether there is any major difference between the two fibres, each showing extremely low coefficients of friction both with and against the scales.

The main point emerging from these results is that it is not necessary to treat the fibres themselves in order to obtain reduced values for their directional frictional effects. Treatment of the smooth horn surface with the unshrinkable reagents will do this. These findings therefore give support to Martin's view that the imbrication of the scales is not the main factor responsible for the directional frictional effect. The chemical structure of the keratin surfaces appears to be a more important factor in the friction between them.

To make sure that the above changes in frictional properties are due to the actual unshrinkable reagents and not to some effect of the neutralising agents or solvents, a control experiment was carried out. A sample of horn was immersed in carbon tetrachloride at 18–19° C. for one hour and then given the same neutralising treatment as in the sulphuryl chloride process described earlier. The results of frictional measurements made with the same fibres on the horn before and after treatment are given in Table 3.

It can be seen that there is no alteration in frictional properties, which proves that the changes recorded above cannot be explained simply by an action of the solvent or neutralising agents.

TABLE 2.

Effect of Horn Treatment on Frictional Measurements (Fibres Untreated).

Fibre.	Horn.	Treatment of Horn.	μ1.	μ2.	D.F.E.
No. 1	Sample A.	Untreated.	0·34	0·11	0·51
No. 2	,,	,,	0·37	0·24	0·21
No. 3	,,	,,	0·40	0·14	0·48
No. 1	Sample A.	Sulphuryl chloride.	0·04	0·04	0
No. 2	,,	,, ,,	0·09	0·07	0·13
No. 3	,,	,, ,,	0·06	0·05	0·09
No. 4	Sample B.	Untreated.	0·31	0·14	0·38
No. 5	,,	,,	0·28	0·15	0·30
No. 6	,,	,,	0·34	0·16	0·36
No. 4	Sample B.	Alcoholic caustic potash.	0·14	0·10	0·17
No. 5	,,	,, ,, ,,	0·14	0·11	0·12
No. 6	,,	,, ,, ,,	0·14	0·12	0·08
No. 7	Sample C.	Untreated.	0·34	0·14	0·42
No. 8	,,	,,	0·42	0·16	0·45
No. 9	,,	,,	0·35	0·14	0·43
No. 7	Sample C.	Aqueous bromine.	0·07	0·07	0
No. 8	,,	,, ,,	0·08	0·05	0·23*
No. 9	,,	,, ,,	0·06	0·05	0·09
No. 23	Sample D.	Untreated.	0·25	0·09	0·47
No. 24	,,	,,	0·32	0·04	0·78
No. 25	,,	,,	0·36	0·13	0·47
No. 23	Sample D.	Aqueous chlorine.	0·03	0·02	0·20*
No. 24	,,	,, ,,	0·04	0·02	0·33*
No. 25	,,	,, ,,	0·04	0·04	0
No. 26	Sample E.	Untreated.	0·31	0·09	0·55
No. 27	,,	,,	0·32	0·12	0·46
No. 28	,,	,,	0·40	0·18	0·38
No. 26	Sample E.	Chlorine in carbon tetrachloride.	0·04	0·02	0·33*
No. 27	,,	,,	0·09	0·05	0·29*
No. 28	,,	,,	0·10	0·06	0·25*

* As explained in the text, these high figures are not significant as the actual frictional values are so low.

TABLE 3.

Effect on Frictional Measurements of Treatment in Carbon Tetrachloride.

Fibre.	Treatment of Horn.	μ1.	μ2.	D.F.E.
No. 11	Untreated.	0·43	0·17	0·43
No. 12	,,	0·34	0·13	0·45
No. 13	,,	0·36	0·15	0·41
No. 11	Carbon tetrachloride.	0·43	0·18	0·41
No. 12	,, ,,	0·36	0·13	0·47
No. 13	,, ,,	0·34	0·13	0·45

The second series of experiments was planned to study the effect of fibre treatment on the directional frictional effect, the horn remaining untreated. The results obtained from these experiments can therefore be used as a basis for comparison with those of earlier workers who have treated the fibres only. The present experiments have the advantage that the measurements were carried out on the same fibres both before and after the various treatments. This procedure is desirable, as it has been found that the variations in frictional properties shown by fibres from the same origin can at times be quite substantial. The results of these experiments are given in Table 4.

TABLE 4.

Effect of Fibre Treatment on Frictional Measurements (Horn Untreated).

Fibre.	Horn.	Treatment of Fibre.	$\mu 1$.	$\mu 2$.	D.F.E.
No. 14	Sample F.	Untreated.	0·35	0·15	0·40
No. 15	,,	,,	0·24	0·13	0·30
No. 16	,,	,,	0·37	0·14	0·45
No. 14	Sample F.	Sulphuryl chloride.	0·25	0·23	0·04
No. 15	,,	,, ,,	0·28	0·28	0
No. 16	,,	,, ,,	0·26	0·24	0·04
No. 17	Sample F.	Untreated.	0·39	0·19	0·35
No. 18	,,	,,	0·36	0·14	0·44
No. 40	Sample G.	,,	0·35	0·15	0·40
No. 17	Sample F.	Alcoholic caustic potash.	0·68	0·43	0·23
No. 18	,,	,, ,, ,,	0·67	0·41	0·24
No. 40	Sample F.	,, ,, ,,	0·65	0·46	0·17
No. 20	Sample F.	Untreated.	0·36	0·14	0·44
No. 21	,,	,,	0·34	0·15	0·39
No. 22	,,	,,	0·33	0·13	0·44
No. 20	Sample F.	Aqueous bromine.	0·22	0·20	0·05
No. 21	,,	,, ,,	0·20	0·17	0·08
No. 22	,,	,, ,,	0·23	0·14	0·24
No. 25	Sample G.	Untreated.	0·40	0·15	0·45
No. 34	,,	,,	0·29	0·15	0·32
No. 35	,,	,,	0·33	0·12	0·47
No. 25	Sample G.	Aqueous chlorine.	0·38	0·30	0·12
No. 34	,,	,, ,,	0·31	0·29	0·03
No. 35	,,	,, ,,	0·34	0·31	0·05
No. 28	Sample G.	Untreated.	0·39	0·16	0·42
No. 31	,,	,,	0·32	0·15	0·36
No. 32	,,	,,	0·36	0·16	0·39
No. 28	Sample G.	Chlorine in carbon tetrachloride.	0·35	0·34	0·01
No. 31	,,	,,	0·43	0·41	0·02
No. 32	,,	,,	0·37	0·35	0·03

The figures show that sulphuryl chloride has greatly raised the with-scale coefficients of friction, and with the exception of one fibre (No. 15) there has been a decrease in anti-scale friction. The directional frictional effect approaches zero in each instance. Alcoholic caustic potash has raised the anti-scale coefficients by about 75%, and has more than doubled the with-scale coefficients,

but the directional frictional effect is still substantial. The effect of aqueous bromine is somewhat similar to that of sulphuryl chloride, there being a drop in coefficients of friction against the scales and a slight tendency towards higher with-scale coefficients. There are no significant differences between the two chlorine treatments; both have greatly increased the with-scale coefficients and the anti-scale coefficients also tend to rise. The directional frictional effects approach zero for each of the chlorine treatments.

As mentioned earlier in this paper, a point which should not be overlooked is the effect on the frictional results when both rubbing surfaces have been treated with the reagent, which is what occurs in practice. A third series of experiments was therefore undertaken in which fibres and horn were treated by the different unshrinkable processes and the changes in frictional properties observed. The results of these experiments are recorded in Table 5.

TABLE 5.

Effect of Fibre and Horn Treatment on Frictional Measurements.

Fibre.	Horn.	Treatment of Fibre and Horn.	$\mu 1$.	$\mu 2$.	D.F.E.
No. 1	Sample A.	Untreated.	0·34	0·11	0·51
No. 2	,,	,,	0·37	0·24	0·21
No. 3	,,	,,	0·40	0·14	0·48
No. 1	Sample A.	Sulphuryl chloride.	0·12	0·10	0·09
No. 2	,,	,, ,,	0·11	0·11	0
No. 3	,,	,, ,,	0·11	0·10	0·05
No. 4	Sample B.	Untreated.	0·31	0·14	0·38
No. 5	,,	,,	0·28	0·15	0·30
No. 6	,,	,,	0·34	0·16	0·36
No. 4	Sample B.	Alcoholic caustic potash.	0·45	0·30	0·20
No. 5	,,	,, ,, ,,	0·41	0·29	0·17
No. 6	,,	,, ,, ,,	0·50	0·29	0·27
No. 7	Sample C.	Untreated.	0·34	0·14	0·42
No. 8	,,	,,	0·42	0·16	0·45
No. 9	,,	,,	0·35	0·14	0·43
No. 7	Sample C.	Aqueous bromine.	0·11	0·09	0·10
No. 8	,,	,, ,,	0·08	0·08	0
No. 9	,,	,, ,,	0·05	0·04	0·11
No. 25	Sample D.	Untreated.	0·36	0·13	0·47
No. 34	Sample G.	,,	0·29	0·15	0·32
No. 35	,,	,,	0·33	0·12	0·47
No. 25	Sample D.	Aqueous chlorine.	0·04	0·02	0·33*
No. 34	,,	,, ,,	0·02	0·01	0·33*
No. 35	,,	,, ,,	0·03	0·03	0
No. 28	Sample E.	Untreated.	0·40	0·18	0·38
No. 31	Sample G.	,,	0·32	0·15	0·36
No. 32	,,	,,	0·36	0·16	0·39
No. 28	Sample E.	Chlorine in carbon tetrachloride.	0·10	0·06	0·25*
No. 31	,,	,,	0·14	0·06	0·40*
No. 32	,,	,,	0·13	0·07	0·30*

* As explained in the text, these high figures are not significant, as the actual frictional values are so low.

These results show that when both surfaces have been treated with either sulphuryl chloride or any of the three halogen processes, the coefficients of friction both with and against the scales drop to extremely low values. The high directional frictional effects given for some of the chlorine treated fibres in Table 5 are due only to slight variations in actual frictional values. Little significance should be attached to the figures for directional frictional effect when dealing with such low coefficients of friction, and it is the actual values of the coefficients that need to be considered. With this in view, the results clearly show that sulphuryl chloride and the halogens substantially reduce the anti-scale and with-scale coefficients to approximately the same values. Alcoholic caustic potash, on the other hand, increases the coefficient of friction against the scales by about 50% and approximately doubles the coefficient of friction with the scales. Its effect is therefore different from that of each of the other reagents. In further support of this contention it has been observed that when a sample of horn is treated with sulphuryl chloride the surface becomes soft and gelatinous during the treatment. Also in the treatment of horn samples with each of the three halogen processes a similar surface effect occurs during the rinse with sodium bicarbonate solution. On the other hand, with alcoholic caustic potash no such effects are noted at any stage of the treatment.

Speakman and Goodings (1926) have recorded the formation of a jelly layer between the cortex and cuticle of wool fibres by the consecutive action of aqueous chlorine and soap or soda (the Allworden reagent). Our observations on horn therefore agree with their results on wool fibres in showing that subsequent treatment with alkali is necessary in order to produce gelatinisation during halogen treatment. From the observations recorded above that the sulphuryl chloride solution on its own will gelatinise horn surface it should follow that the fibre surfaces are gelatinised in this reagent prior to their treatment with alkali. Alcoholic caustic potash on the other hand should not produce any surface gelatinisation of the fibres.

Conclusions.

The results of the present experiments show that it is not necessary to alter the physical structure of the fibre scales in order to reduce their directional frictional effect on a smooth keratin surface. Treatment of the keratin surface alone with certain of the unshrinkable reagents will bring about the necessary reduction. These findings therefore support the views of Martin (1944) in indicating that the directional frictional effect is not simply the physical result of scaliness. They also show that when dealing with fibre surfaces in which the coefficients of friction are very low, the directional frictional effect is not as important in interpreting results as the actual value for the coefficients of friction in each direction.

Finally, they emphasise the need to have both keratin surfaces treated by the different reagents when observing the effect of the latter on the wool fibre surface. With both surfaces treated it has been found that all the unshrinkable reagents excepting alcoholic caustic potash markedly reduce the with-scale and anti-scale coefficients. Alcoholic caustic potash, on the other hand, increases the value of each.

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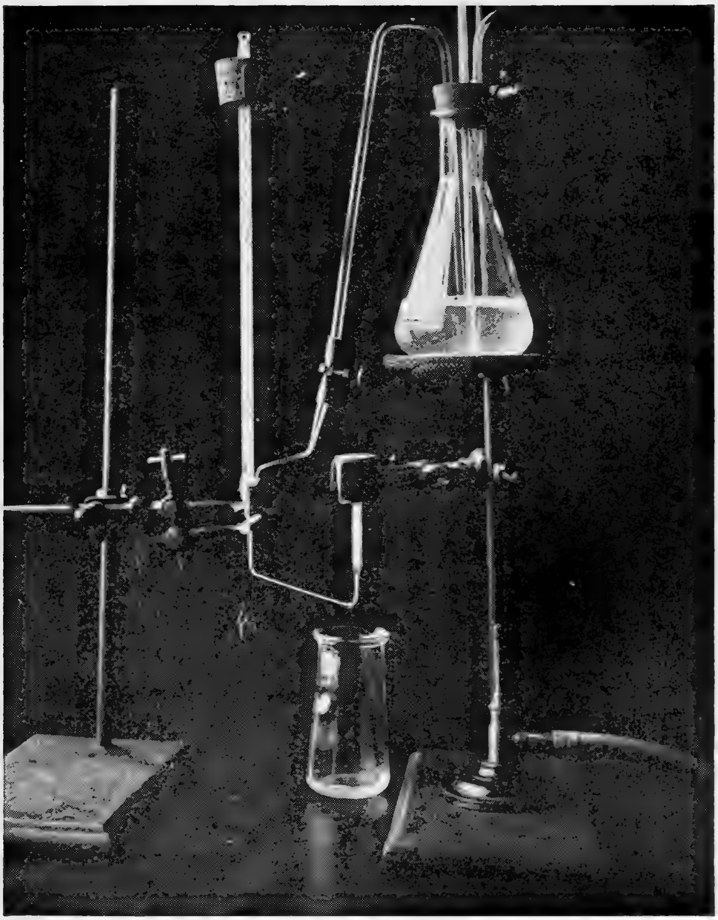

Photograph of the Apparatus Used in Frictional Measurements.

A STUDY OF THE REFLECTION OF LIGHT IN THE CASE OF THREE HOMOGENEOUS, ISOTROPIC, NON-CONDUCTING MEDIA IN SUCCESSIVE CONTACT.

By J. BANNON, B.Sc., F.Inst.P.

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In recent years considerable development has taken place in the production of anti-reflection films on such surfaces as glass. By means of the evaporation process, films, having a variety of properties and a high degree of uniformity, can be deposited. As a consequence, evaporated films have assumed a great importance, both in the world of commerce and in the research laboratory.

These films are produced from a number of metallic fluorides. For instance, calcium fluoride will give a soft film with a refractive index n_D equal to $1 \cdot 26$ ca. (Bannon, 1945)[1] ; cryolite a rather soft film having n_D equal to $1 \cdot 34$ ca., and magnesium fluoride a very hard and water-resistant film, with n_D varying from $1 \cdot 36$ to $1 \cdot 38$ ca., according to the method of evaporation and treatment. A film, developed by the author, called "crycal" (a mixture of cryolite and calcium fluoride) has a value of n_D equal to $1 \cdot 35$ ca., is very hard and is about as resistant as cryolite to water (Bannon, 1944).

The fraction of monochromatic light energy reflected from a film coated glass surface depends on the refractive indices of the film and the glass and on the optical thickness of the film for that particular wavelength. In this paper a mathematical study is presented of the reflection of light, where there are three homogeneous, isotropic and non-conducting media in successive contact. The theory will be applicable to the case of metallic fluoride films on glass surfaces, if the films are homogeneous, isotropic and non-conducting.

From their great transparency and a consideration of the materials from which they are produced, as well as from direct tests, there is little doubt that these films are non-conducting. The author is at present carrying out research on the structures of some metallic fluoride films, and the evidence, so far, indicates that these films are isotropic, as they appear to be made up of minute crystals in random orientation. There may be an orientation in the first few molecules of thickness deposited on the glass, as in the case of the monomolecular built-up films of Blodgett (Holley and Bernstein, 1936). But such an orientation, confined to a relatively very small thickness, will not affect the present treatment. Neither will a variation in film density affect the treatment, if this variation is confined to a thickness of a few molecules at the film glass boundary. From measurements of refractive indices, using films of varying thicknesses, it does not seem likely that there is much departure from homogeneity throughout the film thickness, at least in the case of crown glasses.

A paper will be presented later, by the author, on the structure and homogeneity of evaporated metallic fluoride films.

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[1] In a recent letter to *Nature* the author describes the production of "hard" calcium fluoride films.

Two Surfaces in Contact.

The general expression for a plane wave, which propagates itself in a homogeneous, isotropic, non-conducting medium, in the direction of the positive x axis of a rectangular system, is

$$E_x=0 \qquad H_x=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$E_y=\frac{1}{\varepsilon^{\frac{1}{2}}}f\left(t-\frac{x}{v}\right) \qquad H_y=-g\left(t-\frac{x}{v}\right) \quad \ldots\ldots\ldots (2)$$

$$E_z=\frac{1}{\varepsilon^{\frac{1}{2}}}g\left(t-\frac{x}{v}\right) \qquad H_z=f\left(t-\frac{x}{v}\right) \quad \ldots\ldots\ldots\ldots (3)$$

where E and H are, respectively, the electric and magnetic field intensities, f and g are arbitrary functions of a single argument, and ε is the dielectric constant of the medium.

Suppose there are two infinitely thick, homogeneous, isotropic, non-conducting media 1 and 2, in contact, with a plane boundary between them, and suppose a plane wave is travelling in the direction x, which is parallel to AB. (See Figure 1.) Let AB make an angle θ_1 with the normal N_1N_2 to the boundary.

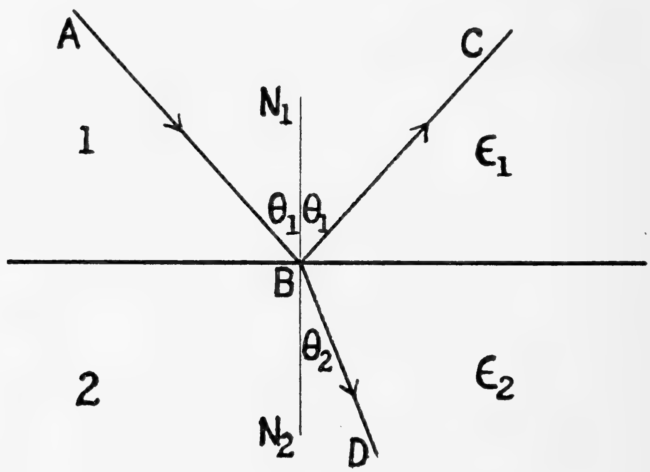

Fig. 1.

In general, when the wave strikes the boundary, it will be partly reflected back into medium 1 and partly refracted into medium 2. The reflected wave will move in the direction BC, which makes an angle θ_1 with BN_1, while the refracted wave will travel in the direction BD, which is inclined to BN_2 at an angle θ_2. BC and BD will be parallel to the plane, which contains AB and BN_1; that is, parallel to the plane of incidence.

If, for the media 1 and 2, the refractive indices are n_1 and n_2, the wave velocities are v_1 and v_2, and the dielectric constants are ε_1 and ε_2 respectively, then the following relations hold:

$$\frac{n_2}{n_1}=\frac{v_1}{v_2}=\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^{\frac{1}{2}}=\frac{\sin\theta_1}{\sin\theta_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If the direction of the y axis of the incident wave is parallel to the plane of incidence, the following relations exist between the wave functions f and g

of the incident wave, and the wave functions f′ and g′ and f_1 and g_1 of the reflected and refracted waves respectively:

$$f' = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_1 \cos \theta_2 + n_2 \cos \theta_1} f = {}_{12}m.f \quad \ldots\ldots (5)$$

$$f_1 = \frac{2n_2 \cos \theta_1}{n_1 \cos \theta_2 + n_2 \cos \theta_1} f = {}_{12}m_1.f \quad \ldots\ldots (6)$$

$$g' = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} g = {}_{12}s.g \quad \ldots\ldots (7)$$

$$g_1 = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2} g = {}_{12}s_1.g \quad \ldots\ldots (8)$$

The terms ${}_{12}m$, etc., above may be called absorption coefficients. If a wave, travelling through medium 2, was incident at an angle θ_2 at the (21) boundary, then, the absorption coefficient, for the refracted f-wave function in medium 1, would be designated by ${}_{21}m_1$. The other absorption coefficients would be similarly designated.

It is evident, from the above four equations, that the f and g functions are independent, and that the magnitude of an f absorption coefficient is, in general, not equal to the magnitude of the corresponding g absorption coefficient.

Three Surfaces in Successive Contact.

Suppose there are three homogeneous, isotropic, non-conducting media in successive contact, and suppose the boundaries between them are plane and parallel. (See Figure 2.) Let media 1 and 3 be infinitely thick, and

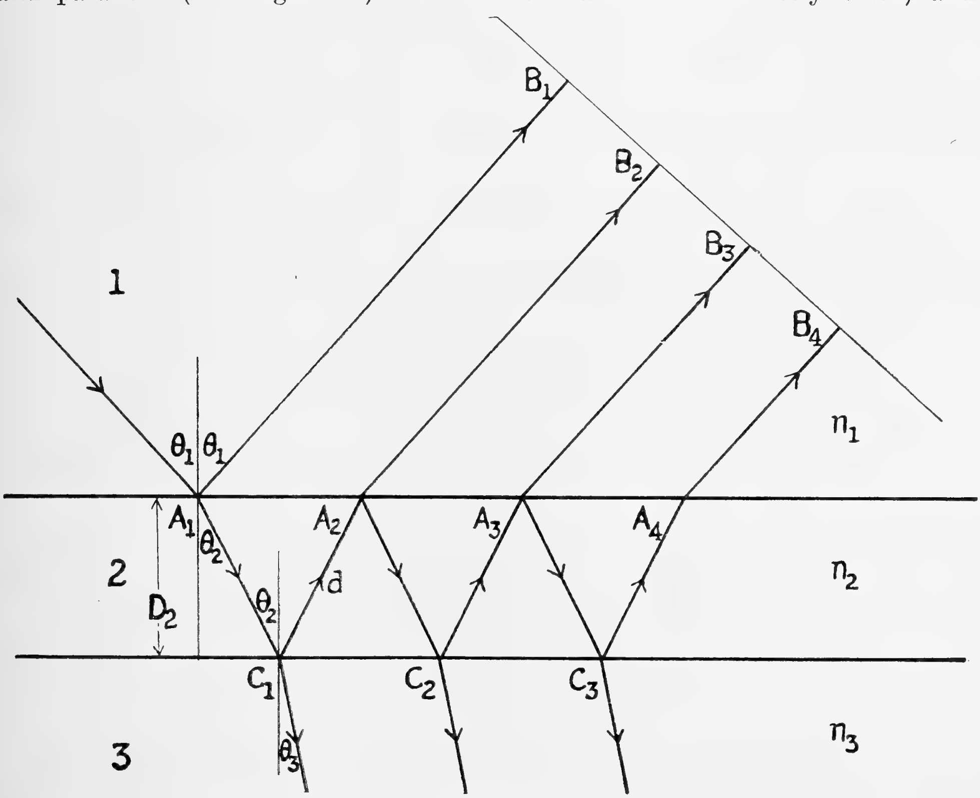

Fig. 2.

medium 2 be of thickness D_2. Let light (represented by a ray) travel through medium 1, and strike the (12) boundary at an angle of incidence θ_1. This ray will be partly reflected along A_1B_1, and partly refracted, at an angle θ_2, into medium 2 along A_1C_1. In medium 2 multiple reflections and refractions will occur. Through medium 1 an infinite number of parallel rays of rapidly diminishing amplitude will travel, and the wave function of the whole of the light returning through medium 1 can be estimated in the way set out below. Medium 2 will be assumed to be sufficiently thin for absorption effects to be neglected.

As in the case above for the two media, let the incident light, which strikes the (12) boundary, be plane. The two wave functions f and g can be treated separately. Considering the incident wave $f\left(t-\frac{x}{v_1}\right)$, let x represent the wave normal at the point A_1, and v_1 the wave velocity in medium 1. If a wave front B_1 B_2 B_3 . . . be selected sufficiently far from the (12) boundary, and if A_1B_1, A_2B_2, A_3B_3, etc., be denoted by r_1, r_2, r_3, etc., respectively, then, the wave function at B_1, of the ray reflected at A_1 along r_1, is

$$_{12}m\ f\left(t-\frac{x}{v_1}-\frac{r_1}{v_1}\right).$$

The wave function at B_2 of the ray travelling along r_2' is

$$_{12}m_1\ _{23}m\ _{21}m_1\ f\left(t-\frac{x}{v_1}-\frac{2d}{v_2}-\frac{r_2}{v_1}\right),$$

where v_2 is the wave velocity in medium 2, and

$$d=A_1C_1=C_1A_2= \quad \ldots \quad (9)$$

The wave function at B_{p+1} of the ray travelling along r_{p+1} is

$$_{12}m_1\ _{23}m^p\ _{21}m^{p-1}\ _{21}m_1\ f\left(t-\frac{x}{v_1}-\frac{2pd}{v_2}-\frac{r_{p+1}}{v_1}\right).$$

Therefore, the wave function, for the whole of the reflected light, whose electric vector vibrates in the plane of incidence, is given by the expression

$$_{12}m\ f\left(t-\frac{x}{v_1}-\frac{r_1}{v_1}\right)+\sum_{p=1}^{\infty}\ _{12}m_1\ _{23}m^p\ _{21}m^{p-1}\ _{21}m_1\ f\left(t-\frac{x}{v_1}-\frac{2pd}{v_2}-\frac{r_{p+1}}{v_1}\right) \quad \ldots (10)$$

From equations (5) and (6) it follows that

$$_{12}m=-_{21}m\ ;\quad _{12}m_1=1+{}_{12}m\ ;\quad _{21}m_1=1-{}_{12}m \quad \ldots \quad (11)$$

$$\text{If } r_1-r_2=e, \quad \ldots \quad (12)$$

$$\text{then } r_1-r_{p+1}=pe \quad \ldots (13)$$

Substituting from equations (4), (11) and (13), expression (10) reduces to

$$_{12}m\ f(\alpha)+\sum_{p=1}^{\infty}\ (1-{}_{12}m^2)\ _{23}m^p\ (-{}_{12}m)^{p-1}\ f(\alpha-p\beta) \quad \ldots (14)$$

$$\text{where } \alpha=t-\frac{x}{v_1}-\frac{r_1}{v_1} \quad \ldots \quad (15)$$

$$\text{and} \quad \beta=\frac{2\frac{n_2}{n_1}d-e}{v_1} \quad \ldots \quad (16)$$

To carry out the summation in expression (14), let f be expanded in the Fourier series

$$\sum_{n=1}^{\infty} a_n \cos(\omega t+\varphi_n) \quad \ldots (17)$$

As the m's in expression (14) vary with the frequency ω, it will be necessary to deal with monochromatic light. This can be done by making $a_n = 0$ for all values of n except 1. By a suitable choice of the time, expression (17) will reduce to

$$a_1 \cos \omega t.$$

As it is easier to work with exponential functions, f can be expressed as follows:

$$f(t) = a_1 e^{i\omega t} \qquad (18)$$

where the real vibration is regarded as the real part of the complex vibration.

By using equation (18), expression (14) reduces to

$${}_{12}m\, a_1 e^{i\omega\alpha} + \sum_{p=1}^{\infty} (1 - {}_{12}m^2)\, {}_{23}m^p\, (-{}_{12}m)^{p-1}\, a_1 e^{i\omega(\alpha - p\beta)}.$$

This reduces to

$$\frac{a_1 e^{i\omega\alpha} ({}_{12}m + {}_{23}m\, e^{-i\omega\beta})}{1 + {}_{12}m\, {}_{23}m\, e^{-i\omega\beta}} \qquad (19)$$

The square of the absolute value of expression (19) will give the intensity of the light returning through medium 1 (reflected light).

This intensity I_f is as follows:

$$I_f = \frac{a_1 e^{i\omega\alpha} ({}_{12}m + {}_{23}m\, e^{-i\omega\beta})}{1 + {}_{12}m\, {}_{23}m\, e^{-i\omega\beta}} \times \frac{a_1 e^{-i\omega\alpha} ({}_{12}m + {}_{23}m\, e^{i\omega\beta})}{1 + {}_{12}m\, {}_{23}m\, e^{i\omega\beta}}.$$

$$\therefore\ I_f = \frac{a_1^2({}_{12}m^2 + 2\,{}_{12}m\, {}_{23}m \cos \omega\beta + {}_{23}m^2)}{1 + 2\,{}_{12}m\, {}_{23}m \cos \omega\beta + {}_{12}m^2\, {}_{23}m^2}.$$

Since the intensity of the incident light is obviously a_1^2, therefore the ratio R_f of the intensity of the reflected light to that of the incident light is

$$R_f = \frac{{}_{12}m^2 + 2\,{}_{12}m\, {}_{23}m \cos \omega\beta + {}_{23}m^2}{1 + 2\,{}_{12}m\, {}_{23}m \cos \omega\beta + {}_{12}m^2\, {}_{23}m^2} \qquad (20)$$

Since the thickness of medium 2 is D_2, it follows from equations (4), (9), (12) and (16) that

$$\beta = \frac{2 n_2 D_2 \cos \theta_2}{n_1 v_1} = \frac{2 D_2 \cos \theta_2}{v_2} \qquad (21)$$

Since $\frac{\omega}{2\pi} \lambda_2 = v_2$ (22)

where λ_2 is the wavelength of the light in medium 2

$$\therefore\ \omega\beta = \frac{4\pi D_2 \cos \theta_2}{\lambda_2} = \psi \qquad (23)$$

But the path retardation l_2, between any two consecutive rays reflected back into medium 1, on account of medium 2, is given by

$$l_2 = 2 D_2 \cos \theta_2 \qquad (24)$$

$$\therefore\ \omega\beta = \frac{2\pi l_2}{\lambda_2} = \psi \qquad (25)$$

Therefore $\omega\beta$ is the difference in phase between any two such consecutive rays.

Using equation (25), R_f may be expressed as follows:

$$R_f = \frac{({}_{12}m - {}_{23}m)^2 + 4\,{}_{12}m\, {}_{23}m \cos^2 \psi/2}{(1 - {}_{12}m\, {}_{23}m)^2 + 4\,{}_{12}m\, {}_{23}m \cos^2 \psi/2} \qquad (26)$$

By similar reasoning, the ratio R_g of the intensity of the reflected light to that of the incident light for the g-wave is

$$R_g=\frac{({}_{12}s-{}_{23}s)^2+4{}_{12}s\ {}_{23}s\cos^2\psi/2}{(1-{}_{12}s\ {}_{23}s)^2+4{}_{12}s\ {}_{23}s\cos^2\psi/2}\quad\ldots\ldots\ldots\ldots(27)$$

Substituting in equations (26) and (27) from equations (5) and (7) and from two similar equations with respect to a (23) boundary, the following relations are obtained:

$$R_f=\frac{(n_2^2\cos\theta_1\cos\theta_3-n_1n_3\cos^2\theta_2)^2+(n_2^2\cos^2\theta_1-n_1^2\cos^2\theta_2)(n_3^2\cos^2\theta_2-n_2^2\cos^2\theta_3)\cos^2\psi/2}{(n_2^2\cos\theta_1\cos\theta_3+n_1n_3\cos^2\theta_2)^2+(n_2^2\cos^2\theta_1-n_1^2\cos^2\theta_2)(n_3^2\cos^2\theta_2-n_2^2\cos^2\theta_3)\cos^2\psi/2}\quad\ldots\ldots\ldots\ldots(28)$$

and

$$R_g=\frac{(n_1n_3\cos\theta_1\cos\theta_3-n_2^2\cos^2\theta_2)^2+(n_1^2\cos^2\theta_1-n_2^2\cos^2\theta_2)(n_2^2\cos^2\theta_2-n_3^2\cos^2\theta_3)\cos^2\psi/2}{(n_1n_3\cos\theta_1\cos\theta_3+n_2^2\cos^2\theta_2)^2+(n_1^2\cos^2\theta_1-n_2^2\cos^2\theta_2)(n_2^2\cos^2\theta_2-n_3^2\cos^2\theta_3)\cos^2\psi/2}\quad\ldots\ldots\ldots\ldots(29)$$

Let equation (28) be written in the form

$$R_f=\frac{a_f^2+c_f\cos^2\psi/2}{b_f^2+c_f\cos^2\psi/2}\quad\ldots\ldots\ldots\ldots(30)$$

Since the media are non-conducting, n_1, n_2 and n_3 are both positive and real, and, consequently, a_f^2 is less than b_f^2. Also, when negative, c_f is less in magnitude than a_f^2, except when $n_1=n_3$. It then equals a_f^2 in magnitude.

Hence, if c_f is positive, the minimum value of R_f, as D_2 varies, will be a_f^2/b_f^2, and the maximum $(a_f^2+c_f)/(b_f^2+c_f)$.

If c_f is negative, the maximum value of R_f, as D_2 varies, will be a_f^2/b_f^2, and the minimum $(a_f^2+c_f)/(b_f^2+c_f)$.

By the use of equations such as (4),

$$c_f=\frac{n_1^2n_2^2}{16\sin^2\theta_2\sin^2\theta_3}(\sin^2 2\theta_1-\sin^2 2\theta_2)(\sin^2 2\theta_2-\sin^2 2\theta_3)\quad\ldots\ldots\ldots\ldots(31)$$

We shall examine the changes of R_f and R_g, with variation of D_2, in the following cases:

Case 1. $n_1<n_2<n_3$.

Here, c_f is zero if

$$\theta_1+\theta_2=90^\circ\quad\ldots\ldots\ldots\ldots(32)$$

or

$$\theta_2+\theta_3=90^\circ\quad\ldots\ldots\ldots\ldots(33)$$

Combining equations (32) and (33) with equations such as (4), c_f is thus zero if

$$\tan\theta_1=\frac{n_2}{n_1}\quad\ldots\ldots\ldots\ldots(34)$$

or

$$\tan\theta_2=\frac{n_3}{n_2}\quad\ldots\ldots\ldots\ldots(35)$$

Equation (35) can be expressed in the form

$$\sin\theta_2=\frac{n_3}{(n_2^2+n_3^2)^{\frac{1}{2}}}.$$

By using equation (4), this reduces to

$$\sin\theta_1=\frac{n_2n_3}{n_1(n_2{}^2+n_3{}^2)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (36)$$

Consequently, equation (33) will be satisfied if

$$n_2n_3 = \text{or} < n_1(n_2{}^2+n_3{}^2)^{\frac{1}{2}}.$$

That is, if

$$n_2{}^2 = \text{or} < \frac{n_1{}^2\,n_3{}^2}{n_3{}^2-n_1{}^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (37)$$

There will, of course, always be a value of θ_1 to satisfy equation (32).

c_f is positive, then, when θ_1 lies between

$$0 \text{ and } \sin^{-1}\frac{n_2}{(n_1{}^2+n_2{}^2)^{\frac{1}{2}}};$$

c_f is negative when θ_1 lies between

$$\sin^{-1}\frac{n_2}{(n_1{}^2+n_2{}^2)^{\frac{1}{2}}} \text{ and } \sin^{-1}\frac{n_2n_3}{n_1(n_2{}^2+n_3{}^2)^{\frac{1}{2}}};$$

c_f is again positive for values of $\theta_1 > \sin^{-1}\dfrac{n_2n_3}{n_1(n_2{}^2+n_3{}^2)^{\frac{1}{2}}}$, if such values are possible.

Hence, for varying values of D_2, R_f is a maximum, for a constant value of θ_1, which lies between $\sin^{-1}\dfrac{n_2}{(n_1{}^2+n_2{}^2)^{\frac{1}{2}}}$ and $\sin^{-1}\dfrac{n_2n_3}{n_1(n_2{}^2+n_3{}^2)^{\frac{1}{2}}}$ ...... (38)

when $\psi=(2n+1)\pi$, $(n=0, 1, 2, \ldots)$ .... (39)

and a minimum when

$\psi=2n\pi$, $(n=0, 1, 2, \ldots)$ .... (40)

When θ_1 lies outside the limits given in (38), then R_f is a minimum when

$\psi=(2n+1)\pi$, $(n=0, 1, 2, \ldots)$

and a maximum when

$\psi=2n\pi$, $(n=0, 1, 2, \ldots)$.

In the case of R_g, equation (29) may be expressed in the form

$$R_g=\frac{a^2{}_g+c_g\cos^2\psi/2}{b^2{}_g+c_g\cos^2\psi/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (41)$$

The quantity c_g is always positive, and, hence, R_g is a minimum, for a constant value of θ_1, when

$\psi=(2n+1)\pi$, $(n=0, 1, 2, \ldots)$

and a maximum when

$\psi=2n\pi$, $(n=0, 1, 2, \ldots)$.

Case 2. $n_1<n_3<n_2$.

By similar reasoning to the above, in this case, when D_2 varies, R_f is a minimum, for a constant value of θ_1, which lies between the limits given in (38), when

$\psi=(2n+1)\pi$, $(n=0, 1, 2, \ldots)$

and a maximum when

$\psi=2n\pi$, $(n=0, 1, 2, \ldots)$.

When θ_1 lies outside the limits given in (38), R_f is a maximum when

$$\psi=(2n+1)\pi, \qquad (n=0,\ 1,\ 2,\ldots)$$

and a minimum when

$$\psi=2n\pi, \qquad (n=0,\ 1,\ 2,\ldots).$$

In the case of R_g, the quantity c_g is always negative and less in magnitude than a^2_g; hence, for a constant value of θ_1, R_g is a maximum when

$$\psi=(2n+1)\pi, \qquad (n=0,\ 1,\ 2,\ldots)$$

and a minimum when

$$\psi=2n\pi, \qquad (n=0,\ 1,\ 2,\ldots).$$

Case 3. $n_1>n_2>n_3$.

Here, R_f and R_g attain maximum and minimum values under the same conditions as in case 1; also, equations (32) and (33) will always be satisfied.

Case 4. $n_1>n_3>n_2$.

Here, R_f and R_g attain maximum and minimum values under the same conditions as in case 2, and equations (32) and (33) will always be satisfied.

From these cases it is evident that, for the f-wave, the value of c_f is zero, when the light rays are incident at the (12) or the (23) boundary at the Brewster angle corresponding to that boundary. For these two particular directions, R_f is independent of D_2. R_f, for the one direction, is equal to reflection at a (13) boundary, and, for the other direction, at a (12) boundary.

For the g-wave, c_g never becomes zero, and, consequently, R_g is never independent of D_2.

By referring back to equation (23), it is seen that ψ varies with the wavelength of the incident light. Consequently, the conditions expressed by equations (39) and (40) will hold for one particular wavelength only, at any one time. Graphs showing the variations of reflectivity with wavelength in the case of cryolite coated glass surfaces appear in a paper by the author published in 1943 (Bannon, 1943). The angle of incidence θ_1 was taken as zero.

In Figure 3, the percentage reflected energies associated with the f- and g-waves, as well as the percentage total energy, are given in the case where D_2 is constant and equal to $\frac{1}{4}\lambda_2$. In other words, at vertical incidence, ψ equals π. At an angle of incidence θ_1, then, ψ is equal to $\pi\cos\theta_2$. The graphs in Figure 3 are of especial interest, because they are the theoretical curves for dense flint glass surfaces (*a*) uncoated and (*b*) coated with film such as magnesium fluoride. It is evident that, in either case, the total amount of light energy reflected varies very little until the angle of incidence θ_1 exceeds 30°. For this particular case, R_f for the coated glass decreases to a minimum and then increases, while R_g steadily increases for increasing values of θ_1.

In the case of three media, such as we are considering, under certain conditions R_f or R_g may become zero.

R_f Equals Zero.

For $n_1\neq n_2\neq n_3$, R_f is zero, if the numerator of equation (30) is zero. As $c_f\neq 0$, except when equation (32) or (33) is satisfied and as c_f, when negative, is less in magnitude than a_f^2, except when $n_1=n_3$, R_f is, in general, zero only when, simultaneously,

$$\psi=(2n+1)\pi, \qquad (n=0,\ 1,\ 2,\ldots)$$

and

$$n_2^2\cos\theta_1\cos\theta_3-n_1 n_3\cos^2\theta_2=0 \quad \ldots\ldots\ldots\ldots(42)$$

Squaring both sides and substituting for $\sin\theta_2$ and $\sin\theta_3$ their values in terms of $\sin\theta_1$ and the refractive indices, we have

$$n_2^4(1-\sin^2\theta_1)\left(1-\frac{n_1^2}{n_3^2}\sin^2\theta_1\right)=n_1^2\,n_3^2\left(1-\frac{n_1^2}{n_2^2}\sin^2\theta_1\right)^2 \quad \ldots\ldots\ldots (43)$$

On expansion, this equation becomes

$$(n_2^8 n_1^2-n_1^6\,n_3^4)\sin^4\theta_1-n_2^2\{n_2^6(n_1^2+n_3^2)-2n_1^4\,n_3^4\}\sin^2\theta_1+ n_2^4\,n_3^2\,(n_2^4-n_1^2\,n_3^2)=0 \quad \ldots\ldots\ldots\ldots (44)$$

Hence

$$\sin^2\theta_1=\frac{1}{2n_1^2(n_2^8-n_1^4n_3^4)}[n_2^2\{n_2^6(n_1^2+n_3^2)-2n_1^4\,n_3^4\} \pm n_2^4\{n_2^8(n_3^2-n_1^2)^2+4n_1^4\,n_3^4(n_2^2-n_1^2)(n_2^2-n_3^2)\}^{\frac{1}{2}}] \quad \ldots\ldots (45)$$

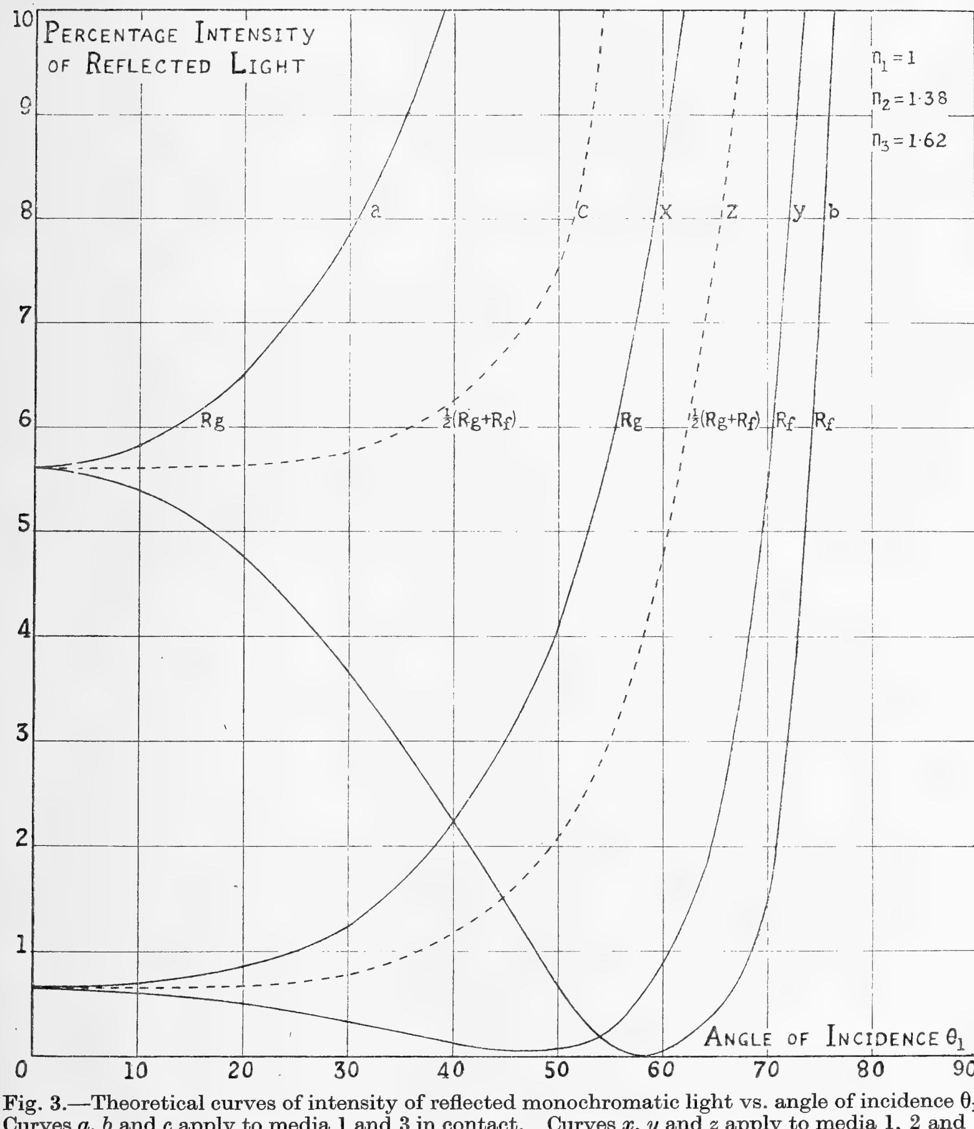

Fig. 3.—Theoretical curves of intensity of reflected monochromatic light vs. angle of incidence θ_1. Curves *a*, *b* and *c* apply to media 1 and 3 in contact. Curves *x*, *y* and *z* apply to media 1, 2 and 3 in successive contact, where D_2 equals $\frac{1}{4}\lambda_2$. All curves intersect the 90 degree ordinate at the point 100.

Let equation (45) be written in the form

$$\sin^2\theta_1=\frac{x\pm y^{\frac{1}{2}}}{z} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (46)$$

when $n_2^2=n_1n_3$

$x=n_2^8(n_3-n_1)^2,$

$y=n_2^{16}(n_3-n_1)^4$ and

$z=0.$

It is easily seen that when $n_2^2>n_1n_3$, x, y and z are each positive.

As n_2^2 decreases in value below n_1n_3, x decreases to zero and then becomes negative. y decreases to zero for a value of n_2^2 equal to $(n_1n_3-\alpha)$. Below this value y becomes negative, reaches a minimum and becomes zero again when n_2^2 equals $(n_1n_3-\beta)$. Below this value of n_2^2, y is positive. $(n_1n_3-\beta)$ is greater than the lesser of the two quantities n_1^2 and n_3^2.

When $n_2^6=\dfrac{2n_1^4\,n_3^4}{n_1^2+n_3^2}$

$x=0$

and $y=4n_1^2\,n_2^4\,n_3^2\,(n_2^8-n_1^4\,n_3^4)\,(n_1^2\,n_3^2-n_2^4),$ $\dots\dots\dots\dots$ (47)

which is negative.

Therefore, when y becomes zero, for $n_2^2=(n_1n_3-\alpha)$, x is still positive. But x is negative when y becomes positive again for values of n_2^2 less than $(n_1n_3-\beta)$.

Also, $x^2-y=4n_1^2\,n_2^4\,n_3^2\,(n_2^8-n_1^4\,n_3^4)\,(n_2^4-n_1^2\,n_3^2)$ $\dots\dots\dots\dots$ (48)

Therefore $x^2=y$ when $n_2^2=n_1n_3$, and $x^2>y$ in all other cases.

When $n_2^2>n_1n_3$, let us consider the equation

$$\sin^2\theta_1=\frac{x+y^{\frac{1}{2}}}{z} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (49)$$

If $x>z$, then no value of θ_1 can satisfy this equation.

If $x<z$, then there is a value of θ_1 if $(z-x)>y^{\frac{1}{2}}$.

On substitution, this condition demands than $n_1n_3>n_2^2$, which by assumption is not so. Hence the equation (49) is not tenable.

Now consider the equation

$$\sin\,^2\theta_1=\frac{x-y^{\frac{1}{2}}}{z} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (50)$$

The numerator $(x-y^{\frac{1}{2}})$ is positive on account of equation (48).

If $x<z$, there obviously is a value of θ_1, which satisfies equation (50).

If $x>z$, then there is a value of θ_1 if

$$(x-z)<y^{\frac{1}{2}};$$

that is, if

$$n_1n_3<n_2^2$$

which by assumption is the case.

Hence equation (50) is tenable.

Similarly equation (50), but not equation (49), is tenable when $n_2^2=n_1n_3$.

When $n_2^2<n_1n_3$, a number of cases must be considered.

Case 1. $n_1n_3>n_2^2\nless(n_1n_3-\alpha)$.

Here $x\pm y^{\frac{1}{2}}$ is positive and z is negative; therefore there can be no value of θ_1.

Case 2. $(n_1n_3-\alpha)>n_2^2>(n_1n_3-\beta)$.

Here, y is negative and, therefore, there can be no value of θ_1.

Case 3. $n_2^2 = \text{or} < (n_1n_3-\beta)$.

Here, x is negative, y is zero or positive, and z is negative.

Let $x=-x'$ and $z=-z'$, where x' and z' are positive.

Then $z'-x'=n_2^8(n_3^2-n_1^2)-2n_1^4\,n_3^4(n_2^2-n_1^2)$.

When $n_3>n_1$, and $n_2^2=n_1n_3$, $(z'-x')$ is positive. For values of n_2^2 between n_1n_3 and n_1^2, $(z'-x')$ will reduce to zero if

$$n_2^8(n_3^2-n_1^2)-2n_1^4\,n_3^4(n_2^2-n_1^2)=0.$$

Substituting the value of n_2^8 from this equation in the expression for y appearing in equation (45), we have

$$y=-2n_1^4\,n_2^8\,n_3^4(n_2^2-n_1^2)(n_1^2-4n_2^2+3n_3^2).$$

Since $n_1n_3>n_2^2>n_1^2$, y is negative.

Therefore, the values of n_2^2, between n_1n_3 and n_1^2, for which $(z'-x')$ can be zero, must lie between $(n_1n_3-\alpha)$ and $(n_1n_3-\beta)$.

In a similar way it can be shown that $(z'-x')$ is positive for values of n_2^2 for which $y=0$.

Also, for $n_2 = \text{or} < n_1$, $(z'-x')$ is positive.

Therefore, for all values of $n_2^2 = \text{or} < (n_1n_3-\beta)$, $(z'-x')$ is positive.

When $n_3<n_1$, and $n_2^2<n_1n_3$, $(z'-x')$ is obviously always positive.

Hence, in all cases $(z'-x')$ is positive for values of $n_2^2 = \text{or} < (n_1n_3-\beta)$.

Let us consider equation (49). This equation can be written in the form

$$\sin^2\theta_1=\frac{-x'+y^{\frac{1}{2}}}{-z'}.$$

$$\therefore\ \sin^2\theta_1=\frac{x'-y^{\frac{1}{2}}}{z'}.$$

As $(x'-y^{\frac{1}{2}})$ is positive by equation (48), and as $z'>x'$, there is a value of θ_1 which satisfies this equation.

Now consider equation (50). This equation can be written in the form

$$\sin^2\theta_1=\frac{-x'-y^{\frac{1}{2}}}{-z'}.$$

$$\therefore\ \sin^2\theta_1=\frac{x'+y^{\frac{1}{2}}}{z'}.$$

A value of θ_1 satisfies this equation if

$$(z'-x')>y^{\frac{1}{2}}$$

that is, if $n_1n_3>n_2^2$, which is the case.

Hence for case 3

$$\sin^2\theta_1=\frac{x\pm y^{\frac{1}{2}}}{z}.$$

R_g EQUALS ZERO.

For $n_1\neq n_2\neq n_3$, R_g is zero if, simultaneously,

$$\psi=(2n+1)\pi, \qquad (n=0,\ 1,\ 2,\ .\ .\ .)$$

and

$$n_1n_3\cos\theta_1\cos\theta_3-n_2^2\cos^2\theta_2=0 \qquad (51)$$

By substitution in equation (51) we have

$$\sin^2 \theta_1 = \frac{n_1^2 n_3^2 - n_2^4}{n_1^2(n_1^2 + n_3^2 - 2n_2^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (52)$$

If $n_2^2 < n_1 n_3$, then both numerator and denominator, on the right-hand side of equation (52), are positive. Moreover, since $(n_2^2 - n_1^2)^2 > 0$,

$$n_1^2(n_1^2 + n_3^2 - 2n_2^2) > (n_1^2 n_3^2 - n_2^4).$$

Therefore, for some value of θ_1, between 0 and $\pi/2$, R_g becomes zero.

If $n_2^2 > n_1 n_3$, then the numerator is negative; and if the denominator is positive, R_g cannot be zero.

If the denominator is negative, then, for R_g to become zero,

$$-n_1^2(n_1^2 + n_3^2 - 2n_2^2) \text{ must be} > (n_2^4 - n_1^2 n_3^2)$$

$$\text{i.e. } -(n_1^2 - n_2^2)^2 \text{ must be} > 0.$$

As this is impossible, R_g cannot be zero when $n_2^2 > n_1 n_3$.

R_f and R_g simultaneously Equal to Zero.

In the general case when $n_1 \neq n_2 \neq n_3$, R_f and R_g cannot be simultaneously zero unless equations (39), (42) and (51) are all satisfied.

That is, unless

$$\psi = (2n+1)\pi, \qquad (n = 0, 1, 2, \ldots)$$

and

$$\cos^2 \theta_2 = \cos \theta_1 \cos \theta_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (53)$$

Squaring both sides in equation (53), and substituting for $\sin \theta_2$ and $\sin \theta_3$ their values in terms of $\sin \theta_1$ and the refractive indices, we have

$$n_1^2(n_2^4 - n_1^2 n_3^2) \sin^4 \theta_1 - n_2^2(n_1^2 n_2^2 + n_2^2 n_3^2 - 2n_1^2 n_3^2) \sin^2 \theta_1 = 0.$$

Therefore

$$\sin^2 \theta_1 = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (54)$$

or

$$\sin^2 \theta_1 = \frac{n_2^2(n_1^2 n_2^2 + n_2^2 n_3^2 - 2n_1^2 n_3^2)}{n_1^2(n_2^4 - n_1^2 n_3^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (55)$$

Equation (55) is not tenable, as the right-hand side is always greater than unity.

Hence, if equation (39) is satisfied, R_f and R_g can be simultaneously zero only when $n_2^2 = n_1 n_3$, and the incidence is vertical.

In the particular case when $n_1 = n_3$, we see, by referring to equations (28), (29), (30) and (41), that

$$c_f = -a_f^2$$

$$\text{and} \quad c_g = -a_g^2.$$

Hence $R_f = R_g = 0$ for all angles of incidence provided that

$$\psi = 2n\pi, \qquad (n = 0, 1, 2, \ldots).$$

In Figure 4 a series of graphs is given showing the variations, with angle of incidence θ_1, of amplitudes of reflected monochromatic light for the f- and g-waves. The reflected amplitudes are given as percentages of the incident amplitude, and are calculated on the assumption that, for each angle of incidence θ_1, the thickness D_2 is such that

$$\psi = (2n+1)\pi, \qquad (n = 0, 1, 2, \ldots).$$

Consequently, the reflected percentage amplitudes A_f and A_g can be expressed as follows:

$$A_f = \frac{100a_f}{b_f}$$

and

$$A_g = \frac{100a_g}{b_g}$$

Throughout the series, $n_1=1$ and $n_3=2$, while n_2 is given in turn the values 1·025, 1·2, 1·5 and 3. It is to be noted that, as θ_1 approaches very closely to 90°, the reflected amplitudes, for both the f- and the g-waves, approach the incident amplitude in magnitude but not in sign. Graph 1 (f) is an instance of particular values of n_1, n_2 and n_3 for which equation (42) is satisfied by two values of θ_1, while graph 1 (g) shows that equation (51) is satisfied by one value of θ_1. For $n_2=1·2$ the reflected amplitude of the f-wave does not become zero for any angle of incidence, while, for $n_2=1·5$ and for $n_2=3$, the amplitude of the g-wave is never zero.

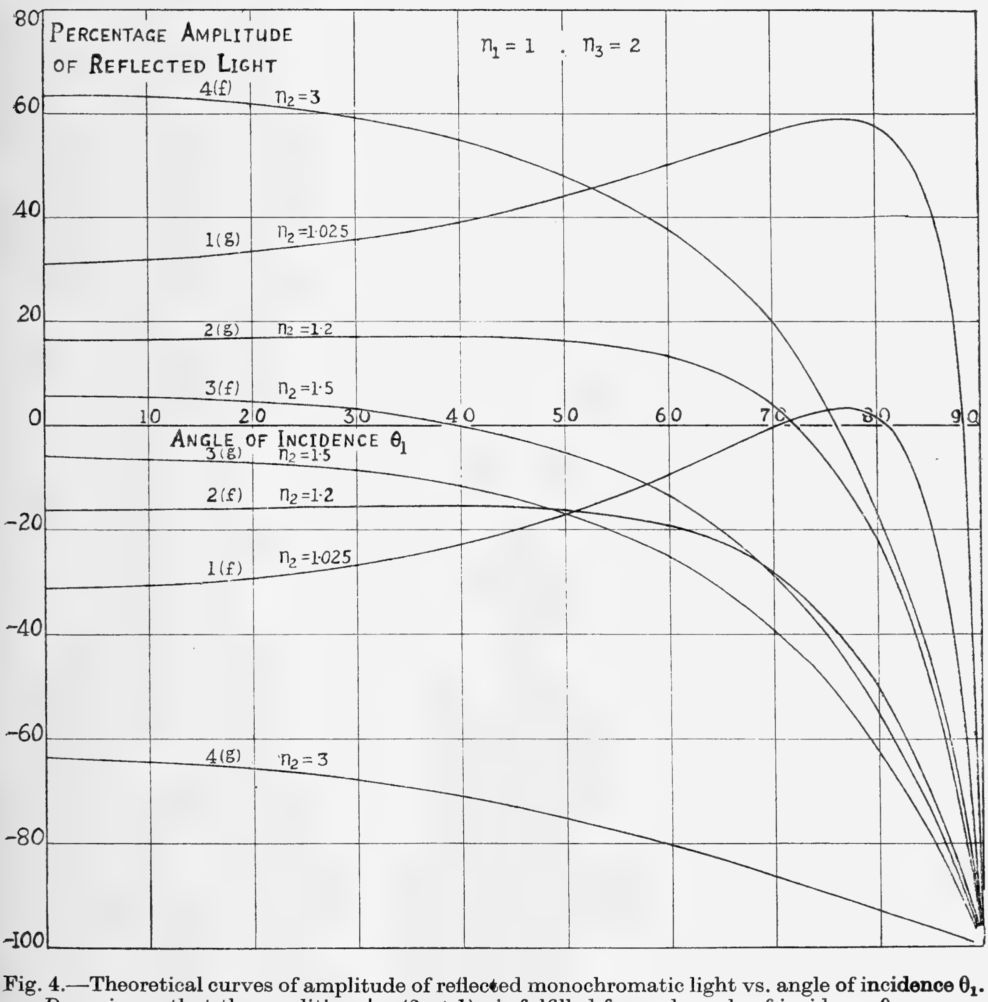

Fig. 4.—Theoretical curves of amplitude of reflected monochromatic light vs. angle of incidence θ_1. D_2 varies so that the condition $\psi=(2n+1)\pi$ is fulfilled for each angle of incidence θ_1.

Conclusion.

When there are two media 1 and 2, separated by a plane boundary and having refractive indices n_1 and n_2 respectively, then, for monochromatic light travelling through medium 1 and incident on the boundary at an angle θ_1,

$$R_f=0 \text{ when } \tan\theta_1=\frac{n_2}{n_1},$$

while R_g is never equal to zero.

When there are three media such as we have dealt with above, R_f is equal to zero for one value of θ_1 between 0 and $\pi/2$, if there simultaneously hold the equation (39), namely

$$\psi=(2n+1)\pi, \qquad (n=0,\ 1,\ 2, \ldots)$$

and the inequality,

$$n_2^2>n_1n_3$$

When $n_2^2=n_1n_3$, the value of θ_1 is zero.

R_f is not equal to zero, for any value of θ_1, if n_2^2 lies between n_1n_3 and $(n_1n_3-\beta)$, where $(n_1n_3-\beta)$ is the smaller of the two real values of n_2^2, which satisfy the equation

$$n_2^8(n_3^2-n_1^2)^2+4n_1^4\,n_3^4(n_2^2-n_1^2)(n_2^2-n_3^2)=0.$$

R_f is equal to zero, for two values of θ_1 between 0 and $\pi/2$, if equation (39) is satisfied and, simultaneously,

$$n_2^2<(n_1n_3-\beta).$$

R_g is equal to zero, for some value of θ_1 between 0 and $\pi/2$, if equation (39) is satisfied and, simultaneously,

$$n_2^2<n_1n_3.$$

When $n_2^2=n_1n_3$, the value of θ_1 is zero.

When $n_1=n_3$, both R_f and R_g are zero, when

$$\psi=2n\pi, \qquad (n=0,\ 1,\ 2, \ldots).$$

If $n_1<n_2<n_3$ and, if D_2 only is variable, then R_f is a maximum when $\psi=(2n+1)\pi$, if θ_1 lies between the limits $\sin^{-1}\dfrac{n_2}{(n_1^2+n_2^2)^{\frac{1}{2}}}$ and $\sin^{-1}\dfrac{n_2n_3}{n_1(n_2^2+n_3^2)^{\frac{1}{2}}}$, and a minimum, if θ_1 lies outside those limits.

When $\psi=2n\pi$, R_f is a minimum, when θ_1 is within the above limits, and a maximum, when θ_1 is outside them.

On the other hand, R_g, for any particular value of θ_1, is a minimum, when $\psi=(2n+1)\pi$, and a maximum, when $\psi=2n\pi$.

When $n_1<n_3<n_2$, the above statements are true, if everywhere the words maximum and minimum are interchanged.

For other relationships between n_1, n_2 and n_3, statements of a similar nature can be made, regarding R_f and R_g.

R_f is independent of the value of D_2, when the light rays are incident at the (12) or the (23) boundary at the Brewster angle corresponding to that boundary.

R_g is never independent of D_2.

Summary.

A mathematical study is presented of the reflection of light, where there are three homogeneous, isotropic, non-conducting media in successive contact. The boundaries between the media are assumed to be plane. Media 1 and 3, of refractive indices n_1 and n_3 respectively, are infinitely thick. Medium 2, of

refractive index n_2, is of thickness D_2, which is sufficiently thin for absorption effects to be neglected.

A plane wave of monochromatic light is assumed to pass through medium 1, and strike the (12) boundary at an angle θ_1. Expressions are derived for the fractional intensities R_f and R_g of the light reflected into medium 1, in the case of the f- and g-waves respectively. The electric vector of the f-wave vibrates in the plane of incidence, while the electric vector of the g-wave vibrates at right angles to that plane.

R_f and R_g are functions of n_1, n_2, n_3, θ_1 and D_2. The changes in these functions, with change in D_2, are examined. The nature of these changes is shown to depend on the relative values of n_1, n_2 and n_3 and, in the case of R_f, on the value of θ_1 also. For certain discreet values of D_2, the functions are analysed, when θ_1 is the variable. It is found that R_f and R_g then depend, in a very striking way, on the relative values of n_1, n_2 and n_3.

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A CONVENIENT VACUUM METHOD FOR THE PREPARATION OF NITROGEN.

By R. C. L. Bosworth, M.Sc., D.Sc.(Adel.), Ph.D.(Cantab.), F.A.C.I., F.Inst.P.

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In the study of the properties of nitrogen on tungsten films by the method of contact potentials, a controllable source of pure nitrogen gas was a primary consideration. Although there are quite a number of methods available for the preparation of this gas from readily procurable chemicals (see, for example, " A Treatise on Chemistry ", by R. E. Roscoe and C. Schorlemner, Macmillan, pp. 485-9), all suffer from the disadvantage that the reactions, once initiated, are difficult, if not impossible, to control. When working under vacuum conditions, an uncontrollable source of any reagent means that the apparatus has to be taken down, reassembled and re-evacuated between each experimental run. The recording of a controllable source of nitrogen may therefore be of some general interest to those engaged in vacuum work.

The mixture used consisted of one part of coarsely crushed ammonium sulphate and two parts of coarse potassium dichromate. This mixture is stoichiometrically equivalent to ammonium dichromate with a slight excess of ammonium sulphate. On gently heating a tube containing this mixture, nitrogen gas (mixed with water vapour) is evolved at a steady rate which may be controlled by controlling the rate of heating. Further, the evolution of nitrogen ceases when the heating ceases, so that the one tube sealed on to a vacuum apparatus can be used to produce small quantities of nitrogen at will over and over again. This behaviour is noteworthy when it is recalled that an equivalent tube of ammonium dichromate, even if largely diluted with such an inert material as sand, behaves with almost explosive violence when heated. The chemistry of the decomposition of ammonium dichromate has recently been treated by Harbard and King (1938).

Apart from water vapour, the gases evolved are also contaminated with traces of oxygen and oxides of nitrogen and therefore need purification before use. The water vapour may be most conveniently removed by passage through a trap immersed in liquid air or some equivalent refrigerating mixture. Since the oxidising gases only occur in traces (unless a deficiency of ammonium sulphate is used in the reaction mixture), they may be removed conveniently and completely by passage over a glowing tungsten filament, running at, say, 2600° K.

A convenient experimental arrangement for the preparation of small quantities of nitrogen for experiments on adsorption or catalysis is given in Figure I. The mixture of ammonium sulphate and potassium dichromate is contained in a thimble B in the vessel A, and is heated by the heater C, a coil of nichrome wire the leads of which are sealed into a pinch in the vessel A. From vessel A the gas passes through the trap D, through the tube E containing the glowing tungsten filament F on to the storage vessel G, from which the gas may be withdrawn as required via the cock I. Both D and E are immersed in a refrigerating mixture whenever the equipment is in operation. The reservoir G is connected to a Pirani gauge H in order to keep a record of the pressure of nitrogen available. By operating filament C from a relay controlled in terms of the resistance of the filament of the Pirani gauge, the pressure in G could be

controlled automatically at any desired figure independent of the amount withdrawn through the cock *I*.

As a means for the laboratory preparation of nitrogen, the heating of a mixture of an ammonium salt with potassium dichromate is, of course, far from new, being described by de Luna (1863) as early as 1863, and recorded in many a textbook on inorganic chemistry. The fact, however, that this particular method of preparation can be controlled under vacuum conditions has, apparently not been stressed before. In the preparation of small quantities of very pure nitrogen, sodium azide offers some advantages, but is not as commonly available as the two salts ammonium sulphate and potassium dichromate. Further, the decomposition of sodium azide, as shown by Tiede (1916), is not readily controllable, and once initiated by heating will proceed at a much lower temperature.

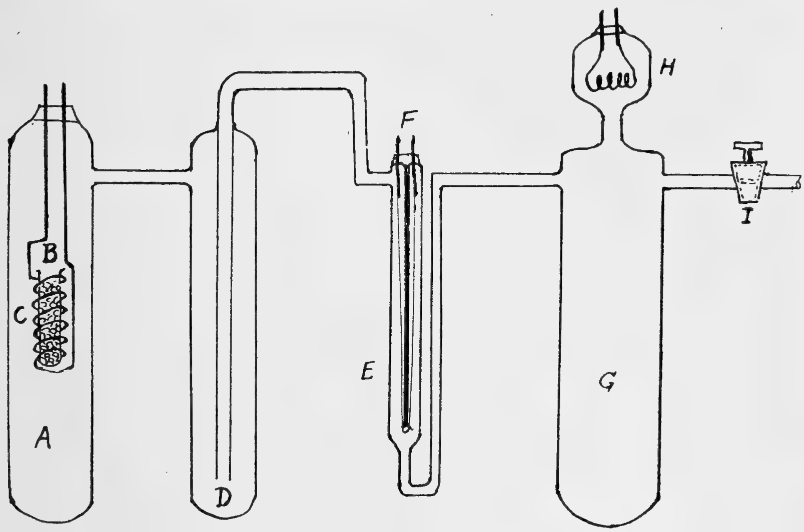

Figure I.

While this paper has been concerned primarily with the utilitarian aspects of a method of preparing nitrogen, the theoretical significance of the reaction is no less interesting. The thermal decomposition of ammonium dichromate may be described as an explosive reaction. The heat set free by the decomposition of any particular molecule is sufficient to supply the activation energy required by each of its neighbours, so that the reaction once initiated cannot be extinguished. (Mulcahy and Yoffe, 1945.) While the activation energy for the decomposition of a mixture of ammonium sulphate and potassium dichromate is probably not very different from that for ammonium dichromate (decomposition sets in at about the same temperature in each case), the rate of reaction in the former case is dominated by a low collision frequency due probably to the slowness of diffusion in the solid state. It is just the time lag due to the slowness of this process which permits local energy excess from the decomposition of any pair of molecules to be dissipated before detonating the neighbours and thus renders the mixture of ammonium sulphate and potassium dichromate non-explosive. The system is clearly one which would repay attention from this point of view.

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QUATERNARY ARSONIUM SALTS AND THEIR METALLIC CO-ORDINATION COMPOUNDS.

Part III. Cobalt.

By F. P. Dwyer, M.Sc.,
N. A. Gibson, M.Sc.,
and R. S. Nyholm, M.Sc.

Manuscript received, September 4, 1945. Read, October 3, 1945.

Some twenty or more tests or modifications of tests have been suggested for the detection of cobalt, but those in general use are confined to the precipitation of the yellow cobalti-nitrites, the formation of the α-nitroso-β-naphthol or the β-nitroso-α-naphthol complex (Feigl and Stern, 1921; Böttger, 1930) and the formation of the blue thiocyanate compound $H_2Co(CNS)_4$ (Vogel, 1901). Rubeanic acid has been suggested by Feigl (1920), but interference by nickel which is normally present as an impurity in cobalt seriously limits its usefulness. Of the former tests, the Vogel test is usually considered the most satisfactory, and many modifications have been applied to raise its specificity and sensitivity (Ditz and Hellebrand, 1935; Kolthoff, 1930; Dwyer, 1936).

In the present investigation, a series of arsonium thiocyanates has been studied as precipitants for cobalt. The blue cobalt compounds formed are highly insoluble in water, but readily soluble in organic solvents such as alcohol, acetone and chloroform. The compounds have the general formula $(R_4As)_2Co(CNS)_4$, and melt sharply to blue liquids. As the molecular weight of the arsonium radical was increased, the solubility decreased, but the colour lightened from royal blue to sky blue. The earlier members were quite soluble in aqueous alcohol to form purplish solutions, indicating dissociation of the complex $Co(CNS)_4''$ ion, and this was confirmed by the observation that addition of ammonium thiocyanate regenerated the blue colour and at the same time precipitated most of the compound.

The sensitivity of the reaction when applied to the detection of cobalt increased with the molecular weight, since it depended chiefly on the marked decrease in solubility and only to a minor extent on the colour of the compounds.

The maximum sensitivity was obtained with tri-p-tolylmethylarsonium thiocyanate, which could detect $0 \cdot 3\ \gamma$ Co/ml. However, triphenylmethylarsonium thiocyanate is the most convenient reagent because its preparation is relatively simple, and in the quantitative colorimetric estimation of cobalt described later, it was used exclusively.

As with the original Vogel test, iron was found to interfere, by the formation of red chloroform-soluble complexes of (probably) the constitution $(R_4As)_3Fe(CNS)_6$, but the interference of this metal could be suppressed by the addition of either sodium ammonium phosphate or sodium fluoride prior to the addition of the arsonium thiocyanate. In this way, it was possible to detect $10\ \gamma$ Co/ml. in the presence of 1,000 times its concentration of iron. Nickel, on the other hand, does not interfere, and cobalt can be readily detected in the presence of large amounts of this metal.

Cobalt may be readily estimated colorimetrically in the presence of large amounts of nickel or small amounts of iron by extraction of the arsonium cobalt

thiocyanate with chloroform followed by comparison with standard cobalt solutions. In the presence of large amounts of iron, however, the precipitated ferric phosphate makes the chloroform extraction difficult, whereas the use of sodium fluoride allows a trace of iron to be extracted, rendering the extract slightly greenish in colour, and hence unable to be matched colorimetrically with the standards.

Experimental.

Bis-di-p-tolyldimethylarsonium Cobaltous Tetrathiocyanate. Di-p-tolyldimethylarsonium iodide (1 gm.) was dissolved in water (100 ml.) with warming, cooled to room temperature, potassium thiocyanate (5 gm.) added, and further water (200 ml.) to keep the arsonium thiocyanate in solution. To this was added in a thin stream with stirring a solution of cobalt sulphate (equivalent to 0·065 gm. of cobalt) and sulphuric acid (1 ml.) in water (50 ml.).

The complex compound separated first as a fine suspension which coagulated on stirring, leaving the supernatant liquid quite clear and colourless. The precipitate was filtered off by suction, and washed with distilled water. As it showed a tendency to form a tar, it was recrystallised as follows: It was dissolved in methyl ethyl ketone (10 ml.) to form a green solution, alcohol (50 ml.) was then added until the solution became a deep blue. Water (300 ml.) was then added until the solution became pink. Finally potassium thiocyanate (5 gm.) was dissolved in the solution, and the precipitated crystalline co-ordination compound filtered off, washed quickly with distilled water, and dried in the desiccator.

The cobalt was determined by decomposition with sulphuric acid, followed by ignition to the oxide Co_3O_4. Residual arsenic was removed by several times moistening the residue with sulphuric acid and re-igniting.

Found: Co=6·9%; As=17·1%.

Calculated for $((C_7H_7)_2(CH_3)_2As)_2(Co(CNS)_4)$: Co=6·8%; As=17·3%.

Sensitivity. The sensitivity tests for cobalt were carried out in the usual manner. The cobalt solutions were prepared from purified $CoSO_4(NH_4)_2SO_4.6H_2O$ (free from nickel), prepared as a stock solution containing 1,000 γ of cobalt/ml. and being normal with respect to sulphuric acid. The arsonium thiocyanate solutions were made up by dissolving 0·5 gm. of the appropriate arsonium iodide in 100 ml. of 10% ammonium thiocyanate solution. Triphenylmethyl-, di-p-tolyldimethyl- and tri-p-tolylmethylarsonium thiocyanates were used as saturated solutions. At the lower limit of the sensitivity tests, the aqueous suspension was extracted with five or six drops of chloroform, and the colour of the lower layer observed.

Test for Interference by Nickel.

A solution of pure, cobalt-free nickel ammonium sulphate (containing approximately 1% nickel) was treated with excess tri-p-tolylmethylarsonium thiocyanate and ammonium thiocyanate, extracted with chloroform, the colourless extract washed, evaporated to dryness, and tested for nickel with dimethylglyoxime. No test was obtained, indicating that the quaternary arsonium thiocyanates do not form chloroform-soluble complexes.

The melting points and sensitivities of the various compounds prepared are shown in Table I below.

Table I.

Compound.	Melting Point.	Cobalt Found.	Cobalt Calculated.	Sensitivity γ Co/ml.
	° C.	%	%	
$((C_6H_5)(CH_3)_3As)_2(Co(CNS)_4)$	89	8·6	8·7	10·0
$((C_6H_5)_2(CH_3)_2As)_2(Co(CNS)_4)$	120	7·2	7·3	0·5
$((C_6H_5)_3(CH_3)As)_2(Co(CNS)_4)$	47	6·1	6·2	0·4
$((C_7H_7)(CH_3)_3As)_2(Co(CNS)_4)$	129	8·2	8·3	1·0
$((C_7H_7)_2(CH_3)_2As)_2(Co(CNS)_4)$	110	6·9	6·8	0·5
$((C_7H_7)_3(CH_3)As)_2(Co(CNS)_4)$	60	6·0	5·8	0·3

Where C_6H_5=the phenyl radical.
C_7H_7=the p-tolyl radical.

Estimation of Cobalt with Triphenylmethylarsonium Thiocyanate.

A solution of pure cobalt ammonium sulphate equivalent to 10,000 γ of cobalt was treated with solutions of sulphuric acid (0·5 ml.), ammonium thiocyanate (5 gm.), sodium phosphate (2 gm.) (to suppress traces of iron), and finally triphenylmethylarsonium iodide (0·3 gm.; 100% excess). The precipitated complex compound was extracted three times with 10 to 15 ml. of chloroform, dried over anhydrous sodium sulphate, and made up to 100 ml. The resultant standard solution had a concentration of the complex compound equivalent to 100 γ of cobalt per ml.

The estimation was carried out by weighing out pure cobalt ammonium sulphate (about 0·1 gm.) accurately, dissolving in water, making up to 100 ml., and taking a 10 ml. aliquot. This solution was then treated exactly as the standard, this time making the chloroform solution up to 25 ml. The intensity of colour of the test solution was then compared with that of the standard in a Klett colourimeter, and the amount of cobalt in the original salt calculated.

Weight of Cobalt Calculated.	Weight of Cobalt Found.	Percentage Error.
gm.	gm.	%
0·01521	0·01529	+0·5
0·01465	0·01462	−0·2

Summary.

The use of quaternary arsonium thiocyanates for the micro-detection of cobalt has been investigated, and it has been shown that these compounds can be used to detect cobalt in a concentration of less than 1 γ of cobalt per millilitre of solution, tri-p-tolylmethylarsonium thiocyanate giving a reaction down to 0·3 γ Co/ml. The reaction may be used in the presence of very large amounts of nickel, and in the presence of a thousandfold concentration of iron, the interference of which can be suppressed with phosphate or fluoride. In the presence of small amounts of iron, the reaction may be used for the colorimetric estimation of cobalt.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT IRIDIUM.

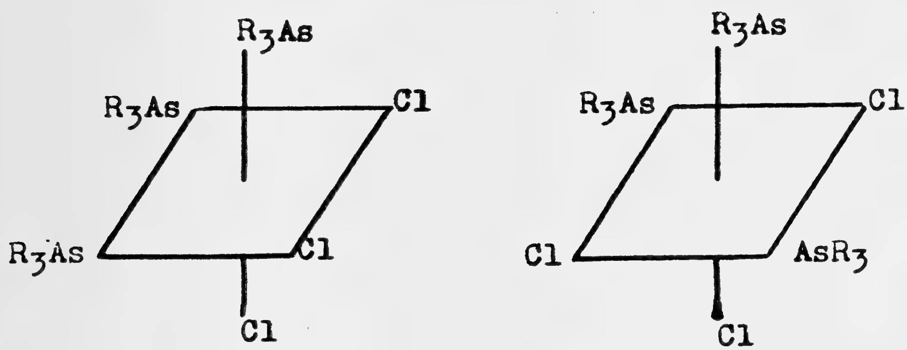
Part III. Complexes of Tertiary Arsines with Trivalent Iridium Halides.

By F. P. Dwyer, M.Sc.,
and R. S. Nyholm, M.Sc.

Manuscript received, September 11, 1945. Read, October 3, 1945.

In a previous paper (Dwyer and Nyholm, 1944) it was shown that trivalent iridium halides in the presence of arsines and hypophosphorous acid gave arsine co-ordinated bivalent iridium compounds of the type $(IrX_2.2ArS.)_2$ and $IrX_2.4Ars$. In the present investigation the reaction between trivalent iridium salts and diaryl-alkyl and dialkyl-aryl arsines has been studied.

When a mixture of iridium trichloride and diphenylmethyl arsine dissolved in aqueous alcohol, containing just sufficient hydrochloric acid to prevent hydrolysis was boiled for a few minutes and then cooled, a yellow oil separated.



(I.) (Ia.)

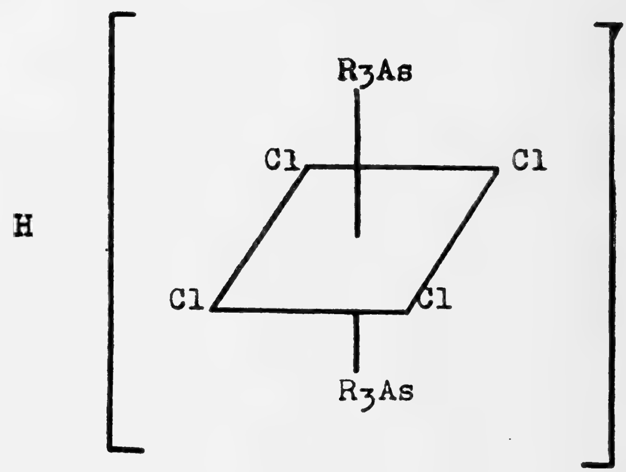
This oil crystallised after trituration with petroleum ether, and when this substance was recrystallised from alcohol the pure compound $IrCl_3.3Ph_2AsMe$ was obtained as a yellow powder easily soluble in organic solvents.

The halogen was not precipitated with alcoholic silver nitrate except on boiling and the compound is thus the covalent hexacovalent complex. The compound had a pronounced odour of arsine, and this, coupled with the poor yields obtained, suggest that the arsine/iridium link is much weaker than in the arsine-rhodium compounds (Dwyer and Nyholm, 1942*a*). This is in accord with the general tendency of the arsine-metal co-ordinate link to become weaker as the metal becomes more basic.

In the presence of a large amount of concentrated hydrochloric acid, and refluxing for some hours, iridium trichloride and the arsine gradually deposited a yellow crystalline compound leaving a red solution, from which water pre-

cipitated a pink crystalline substance, subsequently shown to be an impure specimen of the acid $H(IrCl_4.2Ph_2AsMe)II$.

This substance reacted acid to litmus but was insoluble in caustic alkali. The analysis of the impure substance corresponded to the formula $IrCl_4.2\frac{1}{2}Ph_2AsMe$, but after repeated precipitation from alcohol with hydrochloric acid gave the pure acid $H(IrCl_4.2Ph_2AsMe)$. The pure acid was slightly soluble in warm water, from which it was precipitated with hydrochloric acid ; and gave pink crystalline ammonium and pyridinium salts by treatment with ammonium chloride or pyridinium chloride. It probably arises from chloriridous acid by replacement of two of the chlorine atoms by the arsine. The original compound would thus appear to be a mixture of this acid and the arsonium salt $[Ph_2Me.As.H][IrCl_4.2Ph_2Me.As]$. Burrows and Turner (1921) found that tertiary arsines may yield salts of acids with large anions and isolated for instance $(Ph_2Me.As.H)(BiI_4)$.



(II.)

The yellow crystalline substance obtained during the preparation of the acid had a high melting point and was insoluble in alcohol, but easily soluble in chloroform. In this solvent it was partly dissociated, and if the solvent was evaporated the melting point had fallen 20°, and the substance had a strong odour of arsine. The compound had the empirical formula $(IrCl_3.3Ph_2Me.As)$ but the molecular complexity could not be determined. If monomeric, the compound would be the isomeric form (IA) of the very soluble substance (I) if dimeric the following formulæ may be ascribed $[IrCl.5Ph_2Me.As]$ $[IrCl_5.Ph_2Me.As]$; $[IrCl_2.4Ph_2Me.As][IrCl_4.2Ph_2Me.As]$; $[Ir.6Ph_2Me.As][IrCl_6]$ or the bridged complex $(IrCl_2.3Ph_2Me.As)_2Cl_2$. It is considered unlikely that the compound is the isomeride IA because of its mode of formation from a solution in which the iridium is indubitably present as the chloriridous ion $(IrCl_6)'''$. Assuming, however, that dissociation precedes solution in chloroform, the ionic form $[IrCl_2.4Ph_2Me.As]$ $[IrCl_4.2Ph_2MeAs]$ is probable since the acid $H[IrCl_4.2Ph_2Me.As]$ is obtained from the same preparative mixture, and further it may be transformed into the acid by boiling with alcoholic hydrochloric acid.

The bromo compound $(IrBr_3.3Ph_2MeAs)$ was obtained by refluxing iridium bromide and the arsine in alcoholic solution for a short time, but if the boiling

was prolonged the yellow crystalline compound $(IrBr_2.2Ph_2Me.As)_2$ was precipitated. It is well known that tertiary arsines may function as reducing agents but normally diaryl arsines are quite mild reducing agents and as the authors have found previously (1942*b*) are not sufficiently powerful to reduce Rh^{III} to Rh^{II}. The more difficult reduction of Ir^{III} to Ir^{II} in the present instance must be ascribed to the special circumstance that the compound formed unlike the corresponding chloride and iodide, is highly insoluble (Dwyer and Nyholm, 1944). It should be noted, however, that dialkyl arsines such as dimethylphenyl arsine are much more powerful reducing agents than the diaryl arsines, and it was noted that trivalent iridium salts, notably the iodide, could be reduced to the bivalent state by dialkyl arsines even though the resulting compounds were quite soluble. Hence, it would appear that the low stability of the iridium arsine complexes is also an important factor, since trivalent rhodium compounds are not reduced even by dialkyl arsines.

The bromo-acid $H(IrBr_4.2Ph_2Me.As)$ was readily isolated as pinkish red needles by refluxing rhodium bromide with excess of concentrated hydrobromic acid in the presence of the arsine. All attempts to prepare a high melting form of the bromide analogous to the chloro compound (III) failed.

With the dialkyl arsine, dimethylphenyl arsine, traces only of the low melting compounds $IrX_3.3PhMe_2As$ could be isolated, but the very soluble acids $H(IrX_4.2PhMe_2.As)$ were readily obtained in solution and precipitated as the crystalline ammonium or pyridinium salts.

Experimental.

Tris-diphenylmethyl Arsine Trichloro-iridium (*Low Melting Form*).—Sodium hexachloro-iridate (20 mls.) containing 0·16 g. of iridium was treated with a few drops of dilute hydrochloric acid and alcohol (5 ml.) and boiled until the colour had changed to olive green. The resulting solution of sodium hexachloro-iridite was treated with diphenylmethyl arsine (0·606 g.) and sufficient alcohol to yield one phase on boiling. The solution was boiled for three minutes and then cooled and water added. The precipitated yellow oil, which contained much unreacted arsine, was shaken with petroleum ether, when it solidified to a sticky yellow powder. This substance, crystallised from aqueous alcohol, gave a lemon yellow powder, m.p. 95–96°. The substance was extremely soluble in organic solvents; an alcoholic solution treated with silver nitrate gave no precipitate of the silver halide except on continued boiling.

Found: Ir=18·9%; Cl=10·1%. Calculated for $IrCl_3.3Ph_2Me.As$: Ir=18·71% Cl=10·31%.

(*b*) *High Melting Form*. The sodium hexachloro-iridate solution (20 ml.) as before was reduced with alcohol, and then the arsine and sufficient alcohol to yield one phase added. The mixture was then refluxed for a few minutes, and 10 ml. of alcohol added, followed by concentrated hydrochloric acid until the mixture became just turbid at the boiling point. The refluxing was then continued for a further two hours, during which time a greenish yellow crystalline precipitate gradually came down. The precipitate was removed, and the filtrate was reserved. The substance crystallised in rhombic prisms and plates, m.p. 221°. It was soluble in hot benzene, or cold chloroform. In the latter solvent it apparently underwent dissociation, since the recovered substance melted at 198° and had a strong odour of arsine. The substance slowly dissolved in boiling alcoholic hydrochloric acid to a reddish solution.

Found: Ir=18·9%, 19·0%; Cl=10·3%. Calculated for $IrCl_3.3Ph_2Me.As$: Ir=18·71%; Cl=10·3%.

Hydrogen-bis-diphenylmethylarsine-tetrachloro-iridite. The filtrate from above was diluted carefully with water, when small amounts of yellow compounds were precipitated and then removed. The clear reddish solution was shaken with petroleum ether, and concentrated hydrochloric acid gradually added, when a pink crystalline precipitate appeared. This was washed with petroleum ether and water and dried. The substance at this stage was easily soluble in aqueous alcohol, and reacted acid towards litmus. On analysis it gave Ir=21·2%; Cl=16·5%,

whence the formula is $IrCl_4 2\frac{1}{2}Ph_2Me.As$. The substance was dissolved in alcohol and precipitated with hydrochloric acid. The crystalline precipitate was washed with chloroform and the material redissolved in alcohol and reprecipitated with acid. The pure substance crystallised in pale pink needles and plates, m.p. 144°. It was insoluble in benzene and chloroform, but easily soluble in alcohol or acetone. From the aqueous alcoholic solution addition of ammonium chloride or pyridinium chloride gave the crystalline ammonium and pyridinium salts.

Found: Ir=23·3%; Cl=17·2%. Calculated for $H(IrCl_4.2Ph_2Me.As)$; Ir=23·44%; Cl=17·23%.

Tris-diphenylmethylarsine-tribromo-iridium. This was prepared in the same manner as the chloro compound except that before the reduction of the chloroiridate, potassium bromide (2 g.) was added. The brownish yellow microcrystalline substance obtained in small yield melted at 105°. It was easily soluble in organic solvents, and the halogen was not precipitated with alcoholic silver nitrate except on boiling.

Found: Ir=16·8%. Calculated for $IrBr_3.3Ph_2Me.As$: Ir=16·58%.

Attempts at the preparation of the high melting form were fruitless, and in every case a yellow crystalline precipitate of $IrBr_2.3Ph_2Me.As$ was obtained.

Hydrogen-bis-diphenylmethylarsine-tetrabromo-iridite. Sodium hexachloro-iridate (30 mls.) containing 0·195 g. of iridium was treated with alcohol (50 mls.) and concentrated hydrobromic acid (2 mls.) and refluxed until the reduction was complete. Diphenylmethyl arsine (0·75 g.) was then added and sufficient alcohol to yield one phase on boiling. After refluxing for a few minutes, alcohol (10 mls.) was added, followed by concentrated hydrobromic acid until the solution became just cloudy at the boiling point. The mixture was then refluxed for 30 minutes, when a yellow crystalline precipitate had appeared. This substance ($IrBr_2.3Ph_2Me.As$) was removed and the clear red filtrate diluted carefully with water, when small amounts of a yellow compound were precipitated. Finally the filtrate was treated with hydrobromic acid in the presence of petroleum ether, when it gave a reddish pink crystalline substance. This was purified as with the chloro-acid above. The pure compound crystallised in bright reddish pink plates, m.p. 144°. A solution in aqueous alcohol reacted strongly acid towards litmus.

Found: Ir=19·2%. Calculated for $H(IrBr_4.2Ph_2Me.As)$: Ir=19·26%.

Ammonium Bisdiphenylmethylarsine-tetrabromo-iridite. This salt was prepared by the addition of a saturated solution of ammonium bromide to an aqueous alcoholic solution of the acid above. From the warm solution it crystallised in reddish pink plates, sparingly soluble in water. On heating, ammonia was evolved, and the residual acid then melted at 144°. The compound also liberated ammonia by treatment with caustic soda solution.

Found: Ir=19·2%. Calculated for $NH_4(IrBr_4.2Ph_2Me.As)$: Ir=19·03%.

Tris-diphenylmethylarsine-triodo-iridium (High Melting Form). This substance was prepared by the reaction between potassium iodide and an alcoholic solution of the low melting form of either the chloride or bromide compound. This was conveniently carried out directly on the reaction mixture from which either of these compounds was isolated. The resulting iodo compound crystallised in yellow needles or prisms, m.p. 244°. The compound was sparingly soluble in alcohol, but easily soluble in chloroform. Attempts at the preparation of the low melting form were fruitless.

Found: Ir=14·9%; I=27·2%. Calculated for $IrI_3.3Ph_2Me.As$: Ir=14·79%; I=27·19%.

Pyridinium-bis-dimethylphenylarsine-tetrachloro-iridite. The acid was prepared by treatment of iridium trichloride solution with the arsine (3 mols.) in the presence of excess hydrochloric acid. After cooling and filtration, the pyridinium salt was precipitated by the addition of pyridinium chloride, when it gave pinkish yellow needles. The compound was sparingly soluble in water, but completely soluble in aqueous caustic soda, with the liberation of pyridine. The compound melted at 198°.

Found: Ir=24·7%. Calculated for $(C_5H_6N.H)(IrCl_4Ph.Me_2.As)$: Ir=24·79%.

Pyridinium-bis-dimethylphenylarsine-tetrabromo-iridite. The acid, which was too soluble to be isolated, was obtained in the usual way in the presence of excess hydrobromic acid. The

required salt was precipitated as a pinkish brown crystalline powder by the addition of pyridinium bromide. The compound was completely soluble in aqueous caustic soda.

Found: Ir=20·2%. Calculated for $(C_5H_5NH)(IrBr_4.2PhMe_2.As)$: Ir=20·18%.

Ammonium-bis-dimethylphenylarsine-tetrabromo-iridite. Prepared from the acid by the addition of aqueous alcoholic ammonium bromide gave pinkish yellow needles.

Found: Ir=19·1%. Calculated for $NH_4(IrBr_4.2PhMe_2.As)$: Ir=19·03%.

Conclusion.

Iridium trihalides react with tertiary arsines to form either neutral complexes of the type $IrX_3.2AsR_3$, or more readily, especially in the presence of halogen acids, to form stable acids of the type $H(IrX_4.2AsR_3)$ from which ammonium or pyridinium salts may be prepared.

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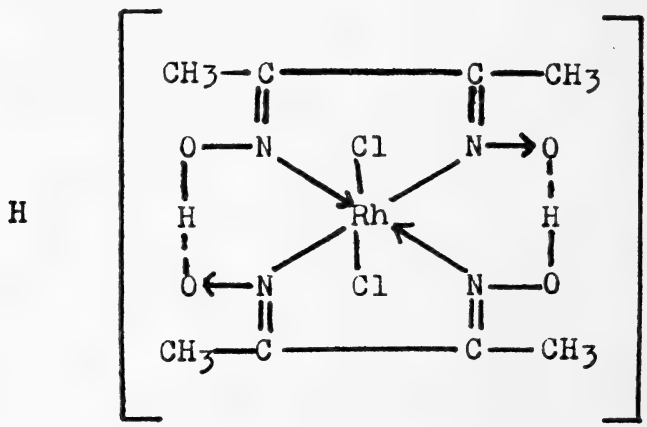
THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART IX. A NOTE ON THE CONSTITUTION OF HYDROGEN-BISDIMETHYLGLYOXIME-DICHLORORHODATE.

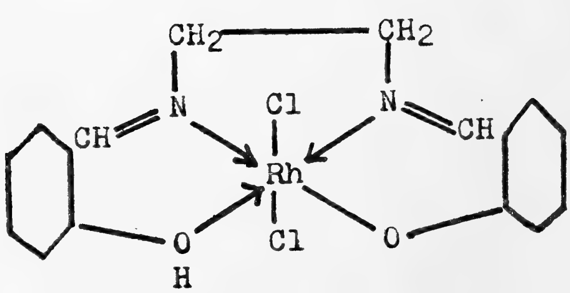
By F. P. DWYER, M.Sc.,
and R. S. NYHOLM, M.Sc.

Manuscript received, September 11, 1945. Read, October 3, 1945.

In a previous paper (Dwyer and Nyholm, 1944) complexes of rhodic halides with dimethyl-glyoxime of the form $H[RhX_2.2C_4H_7O_2N_2]$ were described. The structure (I) ascribed to these compounds, hydrogen bonded two of the hydrogen atoms, and placed the two halogen atoms in the trans positions in the octahedral complex. This formulation was supported by the behaviour of the compounds as monobasic acids and their failure to react with ammonium oxalate to yield oxalato compounds.

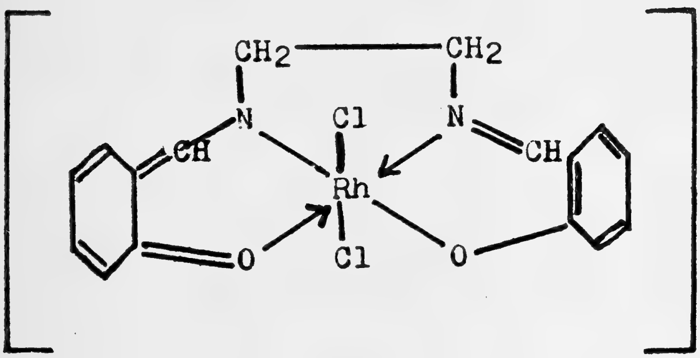


(I).

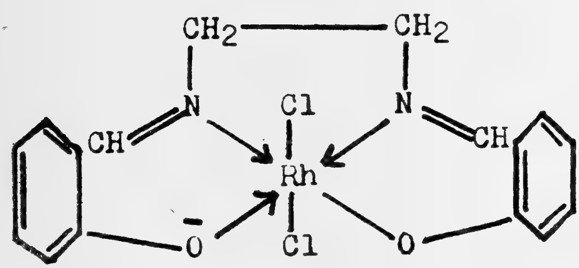


(II)

Assuming the additivity of covalent bond radii, and accepting the standard values (Pauling, 1939), it can be shown that if the bonds to the rhodium are exactly at 90°, for a hydrogen bond O—H—O of 2·5 A.U., the Rh—N—O angle is 113°. This represents a maximum distortion of only 7° from the standard nitrogen bond angle of 120° and assumes that all of the distortion occurs at the nitrogen atom. It is probable that a slight distortion of all relevant bond angles would occur. Similar calculations with nickel dimethyl-glyoxime show that the Ni—N—O bond angle is 125° or a distortion of 5°.



(III)



(IV)

In order to confirm the planar distribution of the two glyoxime groups, attempts have been made to replace them by the reaction with suitable quadridentate groups. Three such groups, all of which function through two primary valencies, and two co-ordinate valencies—ethylenedi-imine-bis-salicyaldehyde (Dubsky and Sokol, 1931), ethylene di-imine-bis-(o, aminobenzaldehyde) (Pfeiffer, 1937) and ethylenedi-imine-bis-acetylacetone (Morgan and Main-Smith, 1925) have been tried. However, the first only of these compounds was found to react, forming a compound $RhX_2.C_{16}H_{15}O_2N_2$ (II). Since the four active groups in this molecule are in the one plane, it follows that the two halogen atoms are in the trans positions, and hence also in the original glyoxime complex which is readily reformed by treatment with excess of dimethylglyoxime. The new compounds are yellow and react acid, yielding, however, violet alkali metal salts. The ion $(RhX_2.C_{16}H_{14}O_2N_2)$ thus apparently exists as a hybrid of the extreme structures III, IV, involving the benzenoid-quinonoid resonance which is the basis of the usual theory of colour.

Experimental.

Ethylenedi-imine-bis-salicyaldehyde Dichlorohodium. The rhodium chloride-glyoxime complex (0·15 g.) (Dwyer and Nyholm, *loc. cit.*) was dissolved in water (10 mls.) containing sodium acetate (2 g.) and then treated with ethylenedi-imine-bis-salicyaldehyde (0·1 g.) in alcohol (10 mls.). The mixture was boiled for 1½ to 2 minutes, when a dark red solution resulted. The mixture was cooled to 0° C. and the precipitated excess ethylenedi-imine-bis-salicyaldehyde filtered off. Addition of cold concentrated hydrochloric acid then precipitated a fine yellow powder, which was coagulated with petroleum ether. The substance decomposed violently on heating without melting. It was soluble in sodium acetate, caustic soda or ammonia to a violet blue solution. The substance was easily soluble in alcohol, but sparingly soluble in water. The yellow saturated solution had a pH of 4·8.

Found: Rh, 23·6%; Cl, 16·1%. Calculated for $RhCl_2.C_{16}H_{15}O_2N_2$: Rh, 23·3%; Cl, 16·1%.

Ethylenedi-imine-bisalicyaldehyde Dibromorhodium. This substance was prepared in the same manner as the chloro-compound, commencing with the rhodium bromide/glyoxime complex. The yellow microcrystalline powder was similarly slightly acid and soluble in alkalis.

Found: Rh, 19·5%; Br, 30·2%. Calculated for $RhBr_2.C_{16}H_{15}N_2O_2$: Rh, 19·45%; Br, 30·2%.

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URIC ACID CONTENT OF HAIR, HORN AND FEATHERS.

By Adolph Bolliger, Ph.D.
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Manuscrip received, September 11, 1945. Read, October 3, 1945.

In a previous communication (Bolliger and Hardy, 1945) it had been stated that considerable amounts of uric acid are present in the hair of the Australian possum (*Trichosurus vulpecula*), the sheep and the rabbit. In the meantime different keratinous skin appendages of a number of other species, including birds, have been tested for uratic compounds and the results are now presented.

Methods.

The methods used were essentially the same as those applied in a previous paper (Bolliger and Hardy, 1945). Hair, horn and feathers, after defatting with carbon tetrachloride and ether, were extracted several times with boiling water till practically all material giving the colorimetric uric acid reaction had been removed. In addition, horn obtained from hoofs, quills, horns and claws was broken up into small particles before extraction with water. Extracting the horn with carbon tetrachloride made it brittle and greatly facilitated its breaking up. For example, fine shavings could be obtained by treating horn in a lathe. The feathers were divided up into barbs and quills (rhachis and calamus) by cutting off closely the barbs from the shafts.

Uric acid was determined by Folin's (1934) colorimetric method, the principle of which is the reduction of tungstic acid by uric acid. In addition the extracts were tested qualitatively with the enzyme uricase and in a number of instances the chromogenic material was isolated in crystalline form.

Results and Discussion.

The results are presented in Table I. They demonstrate that tungstic acid reducing substances were present in every type of hair, quill, horn or feathers obtained from 16 different animal species ranging from birds to various types of mammals, including a monotreme and three marsupials. In the case of the rabbit (Bolliger and Hardy, 1945), dog and cat, the tungstic acid reducing substance was isolated from the hair and found to be uric acid by chemical tests. With other hair, horn and feathers examined the enzymatic reaction with uricase (Blauch and Koch, 1939) was executed as previously described and found to be positive, thus indicating that the tungstic acid reducing substance was also mainly uric acid in these instances.

The amount of uric acid present in hair as determined by colorimetric estimation varied markedly from species to species, but the quantity found was always larger than that present in the blood. Some of the lowest values (9–15 mg. per cent.) have been noticed in the hairs of man, a mammal devoid of uricolytic activity in its tissues, while, rather unexpectedly, mammals with a high uricolytic index frequently exhibited much higher values of uric acid in their hair. The hair on the flanks of the short haired ungulates, cow and horse (Experiments 8 and 9) possessed even lower uric acid values than those found for the hair of man. However, the number of animals tested in any of the orders or families

of mammals is far too small to allow generalisations, and the experiments seem rather to support the theory that the uric acid content of the pelage may perhaps be characteristic of a definite species. In addition, other factors such as the age of the animal or the influence of cutting of hair have still to be investigated,

TABLE I.

Experiment Number.	Animal Species.	Sex.	Integument Type and Location.	Mgm. %.
1	Macaw (*Ara macac*) ..	M.	Blue wing feathers, barbs	136
			,, ,, ,, quills*	9
		F.	Red tail feathers, barbs	130
			,, ,, ,, quills*	12
2	Frogmouth (*Podargus strigoides*).	F.	Wing and tail feathers	61
3	Fowl, white leghorn (*Gallus domesticus*).	M.	Wing feathers, barbs ..	38
			Tail feathers, barbs ..	40
		F.	Wing feathers, barbs ..	36
			Tail feathers, barbs ..	37
			Wing and tail feathers, quills*	14
4	Echidna (*Tachyglossus aculeatus aculeatus*).	M.	Quills	29, 32
		F.	Quills	20, 22
5	Bandicoot (*Perameles nasuta*).	M.	Hairs, abdomen ..	24
			,, back	32
			Claws	19, 19
6	Grey possum (*Trichosurus vulpecula*).	M.	Hairs, abdomen ..	245
			,, flank	160
			,, back	68
		F.	Hairs, abdomen ..	220
			,, flank	150
			,, back	72
7	Ringtail possum (*Pseudochirus laniginosus*).	M.	Hairs, abdomen ..	116
			,, flank	127
			,, back	123
8	Horse (*Equus equis*) ..	F.	Hairs, mane	13
			,, tail	14
			,, body, flank ..	8
			Hoof	13
9	Cow, Guernsey (*Bos taurus*)	F.	Hair, neck mane ..	11
			,, tail	14
			,, body, flank ..	4
10	Goat (*Capra hircus*) ..	M.	,, flank	32
11	Sheep, Merino (*Ovis avies*)	F.	Wool, defatted	15-40
		M.	Horn	4
12	Guinea-pig (*Cavia corbaya*)	M.	Hair, abdomen	144
			,, flank	162
			,, back	163
13	Rabbit, domestic (*Oryctolagus cuniculus*).	M.	Hair, abdomen	466
			,, flank	467
			,, back	521
		F.	Hair, abdomen	383
			,, flank	542
			,, back	466
14	Dog (*Canis domesticus*) ..	M.	Pooled hairs from several dogs.	125
		F.	Pooled hairs from several dogs.	103
15	Cat (*Felis domesticus*)	F.	Hair, abdomen	280
			,, back	252
16	Man, European ..	M.	Hair, scalp	10-15
		F.	Hair (long), scalp ..	9

* Rhachis and calamus.

in as much as it has been observed that the wool of a lamb contained about 100 mg. per cent. (Bolliger and Hardy, 1945), while the fleece of an adult sheep was found to contain only about 15–40 mg. per cent. of uric acid.

The difference between the sexes of the same species, however, was not very significant, although the female sometimes seemed to exhibit slightly lower values (Experiments 6, 13, 14, 16). Frequently, as pointed out previously (Bolliger, 1945), the location of the hairs on the surface of the body was of great importance. In *Trichosurus vulpecula* hairs nearest to the ventral midline contained about three times as much uric acid as those growing on the dorsum. On the other hand, another marsupial of the same family (*Pseudochirus laniginosus*) was found to possess approximately the same amount of uric acid on different parts of the pelage (Experiment 7). Then again the uric acid content of the dorsal hairs of the rabbit was definitely higher than that of the ventral ones (Experiment 12). In the horse and in the cow (Experiments 8 and 9) the flanks were found to contain smaller amounts of uric acid than the dorsum.

Variations in different species were also found to be present in the uricotelic birds which possessed a high uric acid content in the barbs of their feathers, while the quills were found to contain considerably less (Experiments 1 and 3). Nothing definite, however, has yet been observed about variations in different locations of the body of the same bird.

The uric acid content of claws, hoofs and horns may be approximately the same as that found in the hairs of the corresponding animal or less (Experiments 3, 5, 8, 9).

In a previous communication (Bolliger and Hardy, 1945) high uric acid values were also found in the skin of sheep and rabbits which in common with other mammals possess a horny epidermis where these large amounts of uric acid may be situated, though so far no definite proof has been furnished for such an assumption.

Thus, generally speaking, uric acid was found in every keratinous type of integument tested so far, and since many of these are considered to consist solely of keratin it is claimed that uric acid is a definite constituent of this somewhat ill-defined group of proteins. Another explanation, that the uric acid found only adheres or is adsorbed on to the hairs and is actually derived from skin secretions, does not seem tenable in view of the general occurrence of this acid in all types of keratin tested so far, including quills, claws, horn and feathers.

Undoubtedly uric acid is but loosely bound to the keratin molecule and in contrast to the amino acids is readily removed by boiling water. This process, however, also alters some physical characteristics of the protein as probably can best be demonstrated with hair fibres which become stiffer and more brittle.

With regard to the greatly varying amount of uric acid present in the keratin of different animal species, it may be pointed out that this protein in its different biological forms contains remarkably variable quantities of individual amino acids (Harrow and Sherwin, 1935). For example, the cystine content of human hair has been reported to be 14 to 16·5% and that of horse hair 8%, horse hoof 3·2%, and goose feathers 6·4%. In view of this variation of the constituent amino acids a similar alteration in its uric acid content seems feasible.

Finally, it must be pointed out that the figures for uric acid content obtained by the colorimetric method (Folin, 1934) and as enumerated in Table I are of necessity approximate values only, and may, in some instances, contain an experimental error as large as 20%.

Summary.

The uric acid content of feathers, quills, hairs, claws, hoof and horn obtained from 16 different animal species, including three of birds, one monotreme, three

marsupials, four ungulates, two rodents, two carnivores and one primate, was determined.

In every one of these keratinous integuments tested a considerable amount of uric acid was found to be present, ranging from approximately 4 to 540 mg. per cent.

The majority of these determinations were executed on mammalian hair, and it seems likely that the uric acid content of the fur is, with due regard to individual variations, a species characteristic which is only slightly influenced by sex. Hairs from different body regions of the same animal sometimes show marked variations.

From the constant occurrence of uric acid in all types of keratinous integument tested it is concluded that uric acid is a constituent of the protein keratin.

Acknowledgment.

The author wishes to thank Mr. Neil T. Hinks for valuable technical assistance.

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THE VIBRATION FREQUENCIES OF THE TRIGONAL BIPYRAMIDAL MODEL AB_3C_2.

By Allan Maccoll, M.Sc.

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Introduction.

The trigonal bipyramidal structure has been suggested as a result of electron diffraction experiments for the molecules PF_5 (Braune and Pinnow, 1937; Brockway and Beach, 1938), PF_3Cl_2 (Brockway and Beach, 1938), PCl_5 (Rouault, 1938, 1940; Schumaker) in the liquid and gaseous states. Dipole moment measurements of PF_5 (Linke and Ruhrman, 1937) have shown it to possess zero moment. Although a zero moment was found for PCl_5 in solution in CCl_4 (Simons and Jessop, 1931), later work has shown it to possess a small moment in this solution (Trunel, 1936). This has been explained by Moureu, Magat and Wetroff (1937) as being due to the fact that in solution in CCl_4 the PCl_5 molecules do not retain the trigonal bipyramidal structure. The Raman spectrum of PCl_5 has been investigated in the liquid state by Krishnamurti (1930) and by Moureu, Magat and Wetroff (1937). These latter authors determined the polarisation of the Raman lines and found two of the six polarised in accordance with the number predicted for this model by Wilson (1934). Thus both structural and Raman spectral investigations verify the proposed structure.

These molecular data have been used by Stevenson and Yost (1941) to calculate the thermodynamic constants of PCl_5. However, of the eight distinct fundamental frequencies, only six are active in the Raman effect. The two missing frequencies were obtained from the values of the equilibrium constant of the reaction,

$$PCl_3\ (g)+Cl_2\ (g)=PCl_5\ (g)$$

studied by Fischer and Jübermann. In view of this rather doubtful method of deriving the inactive frequencies, it seemed desirable to carry out a normal coordinate treatment of the AB_3C_2 model, which would allow a determination of the force constants and hence of the required frequencies.

The Vibrational Coordinates.

The AB_3C_2 molecule has the symmetry D_{3h}. The internal coordinates, together with the symmetry elements, are shown in Fig. 1. The symmetry elements are:

(1) The identity operation E.

(2) Reflections in the plane σ_h.

(3) Rotations of $2\pi/3$ around the threefold axis C_3.

(4) Rotations of $2\pi/3$ around the threefold improper axis S_3.

(5) Rotations around the twofold axis C_2.

(6) Reflections in the vertical planes σ_v.

The number and type of symmetry coordinates are shown in Table 1.

With the aid of this table the symmetry coordinate may be obtained. The internal coordinates comprise the alterations in the five bond distances (r_i), the three bond angles in $\sigma_h(\alpha_{ij})$, and the six other bond angles (β_i, β_i'). Of the fourteen, only twelve are linearly independent. Rather than arbitrarily neglect

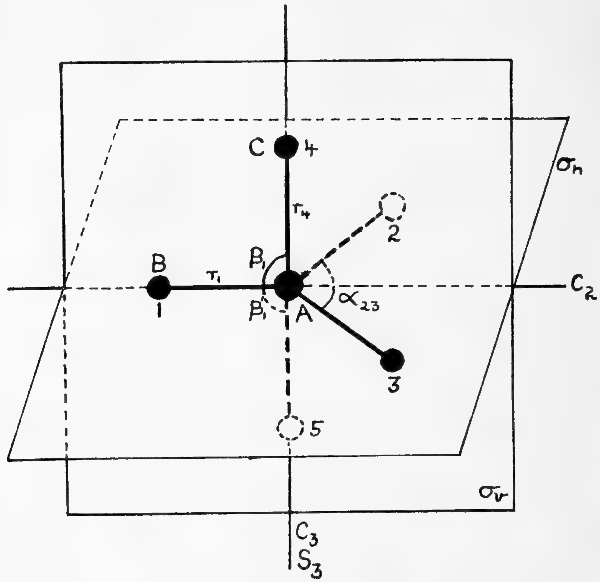

Fig. 1—The symmetry elements and coordinates of AB_3C_2.

Table 1.*

Type.	No.	Symbol.	Symmetry with respect to						Active in	
			E	σ_h	C_3	S_3	C_2	σ_v	Raman.	Infra Red.
A'_1	2	R_1 R_2	+	+	+	+	+	+	Yes.	No.
A''_2	2	R_3 R_4	+	−	+	−	−	+	No.	Yes.
E′	3	R_{5a}, R_{5b} R_{6a}, R_{6b} R_{7a}, R_{7b}	Transform like $x \pm iy$						Yes.	Yes.
E″	1	R_{8a}, R_{8b}							Yes.	No.

* Compare Wilson (1934).

two of them, the technique of Wilson (1941) can be used, namely the selection as two of the symmetry coordinates, the conditions on the α's and β's and making the other symmetry coordinates orthogonal to these. The former may then be neglected as they are identically equal to zero.

The conditional coordinates are:

$$R' = \frac{1}{3^{\frac{1}{2}}}(\alpha_{12}+\alpha_{23}+\alpha_{31})$$

$$R'' = \frac{1}{6^{\frac{1}{2}}}(\beta_1+\beta_2+\beta_3+\beta'_1+\beta'_2+\beta'_3) \quad \text{.....................} \quad (1a)$$

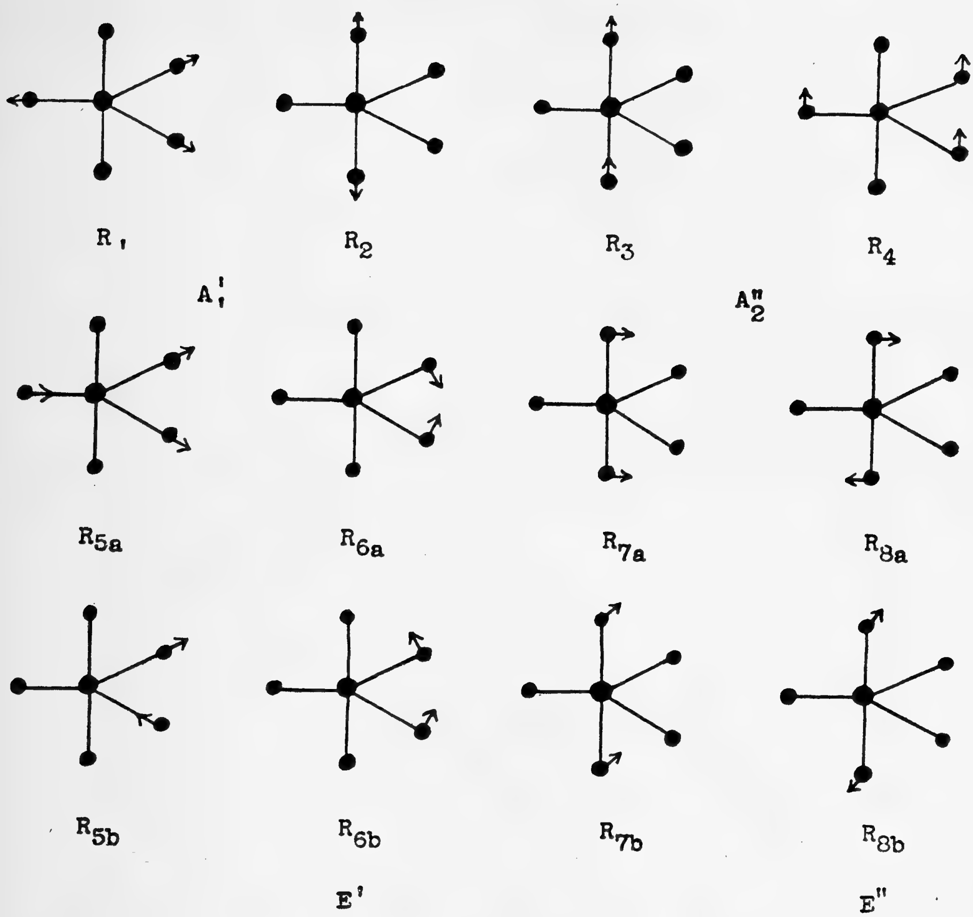

Fig. 2.—The vibrational coordinates of AB_3C_2.

The twelve symmetry coördinates may now be written down:

A'_1 $\quad R_1 = \frac{1}{3^{\frac{1}{2}}}(r_1+r_2+r_3)$

$\quad R_2 = \frac{1}{2^{\frac{1}{2}}}(r_4+r_5)$

A''_2 $\quad R_3 = \frac{1}{2^{\frac{1}{2}}}(r_4-r_5)$

$\quad R_4 = \frac{1}{6^{\frac{1}{2}}}(-\beta_1-\beta_2-\beta_3+\beta'_1+\beta'_2+\beta'_3)$

E′ $$R_{5a} = \frac{1}{6^{\frac{1}{2}}} (-2r_1+r_2+r_3)$$

$$R_{5b} = \frac{1}{2^{\frac{1}{2}}} (r_2-r_3) \qquad (1b)$$

$$R_{6a} = \frac{1}{6^{\frac{1}{2}}} (-2\alpha_{23}+\alpha_{12}+\alpha_{31})$$

$$R_{6b} = \frac{1}{2^{\frac{1}{2}}} (-\alpha_{12}+\alpha_{31})$$

$$R_{7a} = \frac{1}{12^{\frac{1}{2}}} (2\beta_1-\beta_2-\beta_3+2\beta'_1-\beta'_2-\beta'_3)$$

$$R_{7b} = \frac{1}{2} (-\beta_2+\beta_3-\beta'_2+\beta'_3)$$

E″ $$R_{8a} = \frac{1}{12^{\frac{1}{2}}} (2\beta_1-\beta_2-\beta_3-2\beta'_1+\beta'_2+\beta'_3)$$

$$R_{8b} = \frac{1}{2} (-\beta_2+\beta_3+\beta'_2-\beta'_3)$$

The symmetry coordinates form an orthonormal set. The vibrations are shown in Fig. 2.

The Kinetic and Potential Energies and Vibration Frequencies.

The advantage of using symmetry coordinates over internal coordinates is that they enable a factorisation of the secular equation. In the present case the secular equation of the twelfth degree is factored into two quadratic equations corresponding to the A'_1 and A''_2 modes, one repeated cubic and one repeated linear equation corresponding to E′ and E″ modes of vibration respectively.

The method of setting up the secular equation is due to Wilson (1941, 1943, 1939).

The internal coordinates (r_k) are linear functions of the cartesian coordinates (x_i)

$$r_k = \sum_{i=1}^{3n} B_{ki} x_i \qquad (2a)$$

However, they can also be described in terms of vectors ρ_t and $\mathbf{s}_{kt}$ whose components are x_i and B_{ki} respectively

$$r_k = \sum_{t=1}^{n} \mathbf{s}_{kt} \cdot \rho_t \qquad (2b)$$

The kinetic energy matrix $G_{kk'}$ is given by (Wilson, 1939)

$$G_{kk'} = \sum_{t=1}^{3n} \mu_t B_{kt} B_{k't} \qquad (3a)$$

where μ_t is the inverse of the mass of the *t*th atom. In terms of the $\mathbf{s}_{kt}$ vectors, this expression becomes

$$G_{kk'} = \sum_{t=1}^{n} \mu_t \mathbf{s}_{kt} \cdot \mathbf{s}_{k't} \qquad (3b)$$

The computation of the elements of the kinetic energy matrix is simplified by the fact that the $\mathbf{s}_{kt}$ vectors can be expressed in terms of unit vectors along the chemical bonds of the molecule.

Utilisation of the symmetry of the molecule is achieved in the following manner. The symmetry coordinates are defined in terms of the internal co-ordinates by

$$R_j = \sum_k U_{jk}\ r_k \qquad (4a)$$

leading to the new vectors

$$\mathbf{S}^t{}_j = \sum_k U_{jk}\ \mathbf{s}_{kt} \qquad (4b)$$

In terms of these vectors, the kinetic energy matrix breaks up in the same manner as the secular equation, and is given by

$$G_{jj'} = \frac{1}{d} \sum_p \mu_p\, g_p \sum_d \mathbf{S}^t{}_{ja} \cdot \mathbf{S}^t{}_{j'a} \qquad (5)$$

The first summation is over the p non-equivalent atoms, g_p being the number of equivalent atoms of the *p*th set. The second summation is over the d equivalent $\mathbf{S}^t{}_j$ vectors of the irreducible representation of degeneracy d. Where there are a number of equivalent atoms, it thus suffices to calculate the $\mathbf{S}^t{}_j$ vectors for one of the set.

The $\mathbf{s}_{kt}$ vectors are defined in the following manner. If for three atoms $t'-t-t''$ (t being the apex atom) φ is the equilibrium angle and d', d'' are the $t'-t$, $t''-t$ equilibrium distances, the following expressions for the $\mathbf{s}_{kt}$ vectors can be derived.

For changes in the bond distance $t-t'$

$$\mathbf{s}_{kt'} = \mathbf{r}(d'), \qquad \mathbf{s}_{kt} = -\mathbf{r}(d') \qquad (6)$$

For changes in the bond angle φ

$$\mathbf{s}_{kt'} = \frac{\cos\varphi\ \mathbf{r}(d') - \mathbf{r}(d'')}{d' \sin\varphi}$$

$$\mathbf{s}_{kt''} = \frac{\cos\varphi\ \mathbf{r}(d'') - \mathbf{r}(d')}{d'' \sin\varphi} \qquad (7)$$

$$\mathbf{s}_{kt} = \frac{(d' - d''\cos\varphi)\ \mathbf{r}(d') + (d'' - d'\cos\varphi)\ \mathbf{r}(d'')}{d'\, d'' \sin\varphi}$$

$\mathbf{r}(d')$ and $\mathbf{r}(d'')$ are unit vectors at the atom t, directed towards t' and t'' respectively.

In the case of the AB_3C_2 molecule the following vectors are obtained from equations (6) and (7).

Atom A.

$$\mathbf{s}_{r_1A} = -\mathbf{r}_1 \qquad \mathbf{s}_{\beta_1A} = \frac{1}{dd'}\,(d\mathbf{r}_1 + d'\mathbf{r}_4)$$

$$\mathbf{s}_{\alpha_{1j}A} = \frac{3^{\frac{1}{2}}}{d}\,(\mathbf{r}_1 + \mathbf{r}_j) \qquad \mathbf{s}_{\beta'_1A} = \frac{1}{dd'}\,(d\mathbf{r}_1 + d'\mathbf{r}_5)$$

Atom B.

$$\mathbf{s}_{r_1B} = \mathbf{r}_1 \qquad \mathbf{s}_{\beta_1B} = \frac{\mathbf{r}_4}{d}$$

$$\mathbf{s}_{\alpha_{1i}B} = \frac{1}{3^{\frac{1}{2}}d}\,(\mathbf{r}_1 + 2\mathbf{r}_i) \qquad \mathbf{s}_{\beta'_1B} = \frac{\mathbf{r}_5}{d} \qquad (8)$$

Atom C.

$$s_{r_4C} = \mathbf{r}_4 \qquad s_{\beta_1C} = -\frac{\mathbf{r}_1}{d'}$$

$$s_{\alpha_{1j}C} = 0 \qquad s_{\beta'_1C} = 0$$

The $\mathbf{S}^t{}_j$ vectors may now be written down with the aid of (1*a*) and (8). The non-vanishing vectors are:

Atom A.

$$\mathbf{S}^A_3 = -\frac{1}{2^{\frac{1}{2}}}(\mathbf{r}_4-\mathbf{r}_5) \qquad \mathbf{S}^A_{6a} = \frac{1}{2^{\frac{1}{2}}d}(2\mathbf{r}_1-\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^A_4 = -\frac{1}{d}\left(\frac{3^{\frac{1}{2}}}{2}\right)(\mathbf{r}_4-\mathbf{r}_5) \qquad \mathbf{S}^A_{6b} = -\frac{1}{d}\left(\frac{3^{\frac{1}{2}}}{2}\right)(\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^A_{5a} = \frac{1}{6^{\frac{1}{2}}}(2\mathbf{r}_1-\mathbf{r}_2-\mathbf{r}_3) \qquad \mathbf{S}^A_{7a} = \frac{1}{3^{\frac{1}{2}}d'}(2\mathbf{r}_1-\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^A_{5b} = -\frac{1}{2^{\frac{1}{2}}}(\mathbf{r}_2-\mathbf{r}_3) \qquad \mathbf{S}^A_{7b} = -\frac{1}{d'}(\mathbf{r}_2-\mathbf{r}_3)$$

Atom B.

$$\mathbf{S}^B_1 = \frac{\mathbf{r}_1}{3^{\frac{1}{2}}} \qquad \mathbf{S}^B_{6b} = \frac{1}{d}\left(\frac{2}{3}\right)^{\frac{1}{2}}(\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^B_4 = \frac{1}{6^{\frac{1}{2}}d}(\mathbf{r}_4-\mathbf{r}_5) \qquad \mathbf{S}^B_{8a} = -\frac{1}{3^{\frac{1}{2}}d}(\mathbf{r}_4-\mathbf{r}_5)$$

$$\mathbf{S}^B_{5a} = -\left(\frac{2}{3}\right)^{\frac{1}{2}}\mathbf{r}_1 \qquad \ldots\ldots \qquad (9)$$

Atom C.

$$\mathbf{S}^C_2 = \frac{\mathbf{r}_4}{2^{\frac{1}{2}}} \qquad \mathbf{S}^C_{7b} = \frac{1}{2d'}(\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^C_3 = \frac{\mathbf{r}_4}{2^{\frac{1}{2}}} \qquad \mathbf{S}^C_{8a} = \frac{1}{12^{\frac{1}{2}}d'}(2\mathbf{r}_1-\mathbf{r}_2-\mathbf{r}_3)$$

$$\mathbf{S}^C_{7a} = \frac{1}{12^{\frac{1}{2}}d'}(2\mathbf{r}_1-\mathbf{r}_2-\mathbf{r}_3) \qquad \mathbf{S}^C_{8b} = \frac{1}{2d'}(\mathbf{r}_2-\mathbf{r}_3)$$

Use of the expression (9) together with (5) leads to the following values of $G_{jj'}$:

A'_1 mode.

$$G_{11} = \frac{1}{m} \qquad G_{12} = 0$$

$$G_{22} = \frac{1}{m'}$$

A''_2 mode.

$$G_{33} = \left(1+\frac{2m'}{M}\right)\frac{1}{m'} \qquad G_{34} = \frac{2.3^{\frac{1}{2}}}{d\,M}$$

$$G_{44} = \left(1+\frac{3m}{M}\right)\frac{2}{md^2}$$

E′ *mode.*

$$G_{55}=\left(1+\frac{3m}{2M}\right)\frac{1}{m} \qquad G_{56}=\frac{3.3^{\frac{1}{2}}}{2dM} \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$G_{66}=\left(1+\frac{3m}{2M}\right)\frac{3}{md^2} \qquad G_{57}=\frac{3.2^{\frac{1}{2}}}{2d'M}$$

$$G_{77}=\left(1+\frac{2m'}{M}\right)\frac{3}{2d'^2m'} \qquad G_{67}=\frac{9}{6^{\frac{1}{2}}\,dd'M}$$

E″ *mode.*

$$G_{88}=\left(1+\frac{3}{4}\,\frac{md^2}{m'd'^2}\right)\frac{2}{md^2}$$

The potential energy to the valence force approximation is

$$2V=k_r(r^2_1+r^2_2+r^2_3)+k'_r(r^2_4+r^2_5)+d^2k\alpha(\alpha^2_{12}+\alpha^2_{23}+\alpha^2_{13})+dd'k_\beta(\beta^2_1+\beta^2_2+\beta^2_3+\beta'^2_1+\beta'^2_2+\beta'^2_3) \quad \ldots\ldots\ldots\ldots \quad (11)$$

Since the transformation (1*b*) is orthonormal r_i, α_{ij}, β_i, β'_i can be expressed in terms of the R_j, and substitution in (11) leads to

$$2V=k_r(R_1{}^2+R^2{}_{5a}+R^2{}_{5b})+k'_r(R^2{}_2+R^2{}_3)+d^2k_\alpha(R^2{}_{6a}+R^2{}_{6b})+dd'k_\beta(R^2{}_4+R^2{}_{7a}+R^2{}_{7b}+R^2{}_{8a}+R^2{}_{8b}) \quad \ldots\ldots\ldots\ldots (12)$$

Thus the potential energy matrix is given by

$$F_{11}=F_{55}=k_r$$
$$F_{22}=F_{33}=k'_r \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$
$$F_{44}=F_{77}=F_{88}=dd'k_\beta$$
$$F_{66}=d^2k_\alpha$$

Using the values for $G_{jj'}$ and $F_{jj'}$ thus obtained, the secular equation can be written in an expanded form as shown by Wilson (1939). In this manner the following equations are obtained, where

$$\lambda_i=4\pi^2\ c^2\ \nu_1{}^2$$

$$\lambda_1=\frac{k_r}{m} \qquad \lambda_2=\frac{k'_r}{m'}$$

$$\lambda_3+\lambda_4=\left(1+\frac{2m'}{M}\right)\frac{k'_r}{m'}+\left(1+\frac{3m}{M}\right)\frac{2d'k_\beta}{dm}$$

$$\lambda_3\lambda_4=\left(1+\frac{3m}{M}+\frac{2m'}{M}\right)\frac{d'}{d}\,\frac{2k'_rk_\beta}{m^2}$$

$$\lambda_5+\lambda_6+\lambda_7=\left(1+\frac{3m}{2M}\right)\frac{(k_r+3k_\alpha)}{m}+\left(1+\frac{2m'}{M}\right)\frac{3}{2m'}\,\frac{d}{d'}\,k_\beta \quad \ldots\ldots \quad (14)$$

$$\lambda_5\lambda_6+\lambda_5\lambda_7+\lambda_6\lambda_7=\left(1+\frac{3m}{M}\right)\frac{3k_rk_\alpha}{m^2}+\left(1+\frac{3m}{2M}+\frac{2m'}{M}\right)\frac{d}{d'}\,\frac{3k_\beta(k_r+3k_\alpha)}{2mm'}$$

$$\lambda_5\lambda_6\lambda_7=\left(1+\frac{3m}{M}+\frac{2m'}{M}\right)\frac{9}{2}\,\frac{d}{d'}\,\frac{k_rk_\alpha k_\beta}{m^2m'}$$

$$\lambda_8=\left(1+\frac{3md^2}{4m'd'^2}\right)\frac{d'}{d}\,\frac{2k_\beta}{m}$$

By putting $k'_r = k = 0$, these equations reduce to the "in the plane" vibrations of the planar AB_3 molecule investigated by Menzies (1931), Anderson, Lassettre and Yost (1936), and Silver and Shaffer (1941).

It is hoped to apply the treatment of this paper to the assignment of the vibrational frequencies of the PCl_5 molecule.

Summary.

The vibration frequencies of the trigonal bipyramidal AB_3C_2 molecule have been determined in terms of the force constants of the valence force potential function. Expressions for the kinetic energy matrix are reported in terms of the valence coordinates, thus enabling the addition of cross terms to the potential function.

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VOLUME LXXIX

Part IV

A NOTE ON THE PLATINUM DERIVATIVE OF A SUBSTITUTED PYRROMETHENE.

By D. P. MELLOR, D.Sc.,
and J. B. WILLIS, M.Sc.

Manuscript received, October 17, 1945. Read, November 7, 1945.

In a previous communication (Mellor and Lockwood, 1940) it was shown that the nickel compound of 33′55′ tetramethyl 44′ dicarbethoxy pyrromethene was paramagnetic with a moment of 3·2 Bohr magnetons, while the palladium complex was diamagnetic. As may be seen from the formulæ of these compounds, considerable distortion from the planar structure in the metal-nitrogen bonds occurs, owing to the clashing of the α-methyl groups indicated by the asterisks.

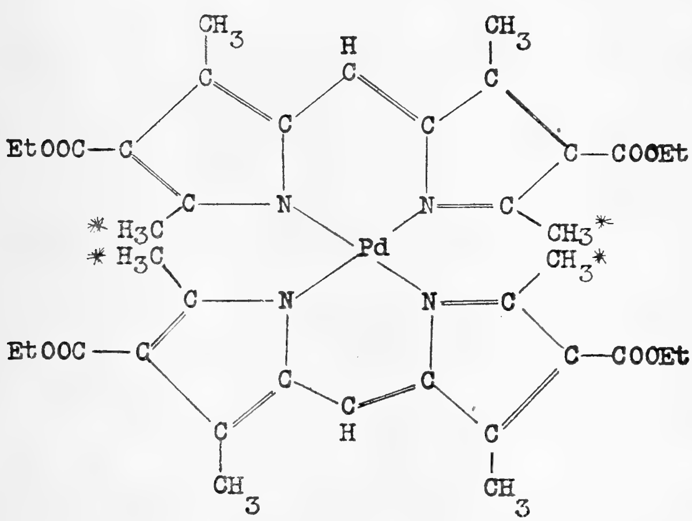

Fig. 1.

The platinum complex has now been prepared in a pure form.

The 33′55′ tetramethyl 44′ dicarbethoxy pyrromethene was prepared as described by Mellor and Lockwood (*loc. cit.*). The preparation of the platinum complex is of interest, however, because it was found that the use of potassium chlorplatinite even in considerable excess did not lead to the formation of a binuclear complex such as was found by Porter (1938) when potassium chlorpalladite was used in place of palladium nitrate.

The platinum complex was prepared by treating the hydrochloride of the base (in alcohol) with sodium acetate and about three times the theoretical amount of potassium chlorplatinite. The solution was gently heated, allowed to stand for half an hour, and the copious precipitate of platinum filtered off.

The complex was recovered from the filtrate by precipitation with water, and recrystallised from chloroform and petroleum ether.

Found: Pt=22·2%. Calculated for $C_{38}H_{46}O_8N_4Pt$: Pt=22·15%.

A large excess of chlorplatinite was found to be necessary owing to the extensive reduction to platinum brought about by the pyrromethene, but as pointed out above, no binuclear compound was formed even with a large excess of chlorplatinite.

The Magnetic Susceptibility and Absorption Spectrum.

Since the platinum complex was found to be diamagnetic like that of palladium, it is inferred that the Pt-N bonds are covalent in character.

In discussing the question whether distortion of metal interbond angles in the Ni, Pd and Pt complexes of this pyrromethene is likely to cause a transition from essentially covalent to ionic bonding two factors must be taken into consideration:

(a) The amount of angular distortion from the planar arrangement of the metal-nitrogen bonds. Other factors being the same, angular distortion decreases with increasing covalent radius of the metal atom.

(b) The position of the atom in the electro-negativity scale. The greater the difference in electro-negativity between the metal and nitrogen, the greater the tendency to form ionic bonds. It may well be that the greater the electro-negativity difference, the less the distortion required to change the character of the metal-nitrogen bonds.

The covalent radii of Ni, Pd and Pt are 1·21, 1·31 and 1·31 A, respectively (Pauling, 1940). Thus less clashing is to be expected in the palladium and platinum compounds than in the nickel compound. For this reason and also because nickel forms ionic bonds more readily than either Pd or Pt,[1] the nickel complex is the only one in which distortion produces a change of bond type.

The absorption spectrum of the platinum complex (in absolute alcohol) taken with a Hilger-Nutting spectrophotometer,[2] showed a narrow band at 487 ± 1 mμ with a molar extinction coefficient of about 20,000. This is at the same wavelength as the band in the palladium complex (Mellor and Lockwood, *loc. cit.*).

Investigations by H. A. McKenzie have shown that the nickel complex of the pyrromethene has an absorption band at 490 mμ in absolute alcohol, and not at 527 mμ as reported by Fischer and Schubert (1924). Thus the abrupt change in the position of the absorption band between the ionic nickel complex and the covalent palladium one pointed out by Mellor and Lockwood is not so pronounced as it was first thought to be.

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[1] It is still problematical whether either of these metals ever forms ionic bonds (as judged by the magnetic criterion). Experiments on K_2PtF_6 are in progress to test the applicability of the magnetic criterion to these metals (Pt and Pd).

[2] We are indebted to Dr. R. Lemberg, of the Royal North Shore Hospital, for making available this instrument.

ON GLACIAL LAKES IN THE KOSCIUSKO REGION.

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Manuscript received, October 5, 1945. Read, November 7, 1945.

INTRODUCTION.

The glacial origin of alpine lakes occurring along the Main Dividing Range near Mount Kosciusko was first recognised by David, Helms and Pittman (1901), who described evidence of comparatively recent glaciation, including moraine-dammed lakes resulting from the action of small valley-glaciers existing at elevations mainly above 6,000 feet. In a later paper, David (1908), recorded additional evidence of glaciation and discussed the origin of the Blue Lake, which he investigated in some detail. Taylor, Browne and Jardine carried out topographical work in 1925, recording further evidence of glaciation. Additional observations in the vicinity of the lakes and over a wide area, including country to the north of Kosciusko, were made by Browne, Dulhunty and Maze in 1944.

The investigations described in the present paper are confined to a detailed study of the nature and origin of the principal glacial lakes: Cootapatamba and Albina on the western side of the Main Divide, the Club Lake and Blue Lake on its eastern side. Hedley Tarn is not included, as it appears preferable to group it with the drained or silt-filled lakes, which, it is hoped, may be the subject of future investigations.

In the case of each of the four lakes examined, a systematic series of soundings was made to obtain bottom contours, and shore-lines were mapped in detail. The valley sides and form and nature of moraines in the vicinity of each lake were studied, and an attempt was made to determine, as accurately as possible, the depth of morainic material damming the water, and the level of solid rock surface beneath the dam in relation to the surface and bottom of the lake.

The maps (Figs. 2 and 4) of the lakes show minor topographical features, such as ridges of morainic material and outcropping rock, in the immediate vicinity of the shorelines, no attempt being made to indicate the steep and in some cases precipitous walls of the depressions in which the lakes are situated. For descriptions and illustrations of major topographical features, reference should be made to Taylor, Browne and Jardine (1925).

Method of Taking Soundings.

The following method was adopted, as the rugged country between the motor road and the lakes presents difficulties in the transport of a boat suitable for taking a systematic series of soundings in the usual way.

Equipment consisted of a float in the form of a flat, one-gallon oil tin with a light 3 in. pulley-wheel and stabilising beam attached to the lower surface (see Fig. 1); a tow-line 1,500 feet long wound on a reel, and knotted every 30 feet; a sounding-line of similar length knotted every foot, and wound on a reel. The tow-line was attached to one end of the float; and the sounding-line, carrying a sinker of about 2 lb. weight, passed over the pulley-wheel beneath the float. The float was placed on the water at a convenient point where the shoreline

passed round a bay or estuary. The operator and assistant, carrying sounding- and tow-line reels respectively, moved away from each other around the shoreline, the two lines being paid out under sufficient tension to keep the sinker up at the pulley-wheel. In this way the float could be manoeuvred to any desired position on the lake. Soundings were made by releasing the sounding line until the sinker left the float, then pulling the line slowly in until it touched the float. This was felt by tension on the line. After several tests the exact point of contact between sinker and float was determined on the sounding line as it passed through the operator's hands. The line was then allowed to run out slowly, one-foot knots being counted until the sinker touched the bottom of the lake. The depth was obtained by the length of line paid out at the shore.

The lines were treated with an oil dressing so that they would float near the surface of the water, facilitating movement of the float, and avoiding error due to sagging. The float was weighted so that as little as possible remained above the surface of the water. This, together with the tension on the lines, successfully prevented the float from drifting in the wind.

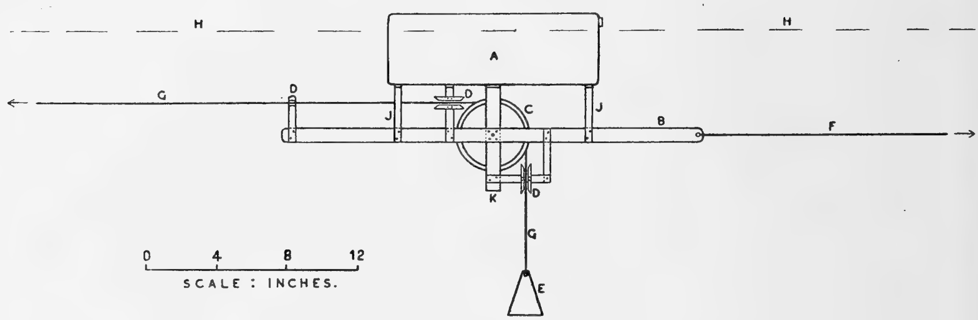

Fig. 1.—Diagrammatic illustration of sounding equipment.

A. Float.	F. Tow-line.
B. Stabilizing beam.	G. Sounding-line.
C. Pulley-wheel.	H. Surface of water.
D. Line guides.	J. Outer beam supports.
E. Sinker.	K. Central beam and pulley-wheel support.

After some practice soundings accurate to within one foot were obtained rapidly and with comparative ease—apart from difficulties experienced in negotiating the rough and boulder-strewn shorelines which occur in places.

At each lake a systematic series of soundings was made along a number of selected lines. The distances between the soundings were measured by the length of tow-line taken in, or let out, by the assistant, while the float was being moved from one point to another along the line. The position of each line of soundings was determined by fixing its terminal points in a shoreline traverse.

The Blue Lake.

The Blue Lake, situated immediately to the south of Mt. Twyman, is the largest, deepest and most important of the glacial lakes. The general features of the lake, and evidence which it bears of recent glaciation, have been described (David, 1908; David, Helms and Pittman, 1901).

The exact shape and size of the lake, together with depth contours and shoreline features, are illustrated in Fig. 2. It is roughly oval in shape, 650 yards long and 450 yards wide, with a surface area of about 39 acres. The total number of 120 soundings taken along nine lines across the lake revealed a maximum depth of about 95 feet over a small area situated towards the south-eastern end.

The deepest sounding recorded was 90 feet, but interpolation in the construction of depth contours indicated an area between 90 and 100 feet deep, probably about 95 feet. This is some 20 feet deeper than the maximum depth of 75 feet recorded by David (1908).

The form of the lake bottom is shown by depth contours in Fig. 2 and sections in Fig. 3. It is evident that the bottom is somewhat irregular, possessing two depressions near the centre and towards the south-eastern end, 85 and 95 feet deep, respectively. On the north-western side there are two small elevated areas standing between 10 and 15 feet above the general level of the bottom.

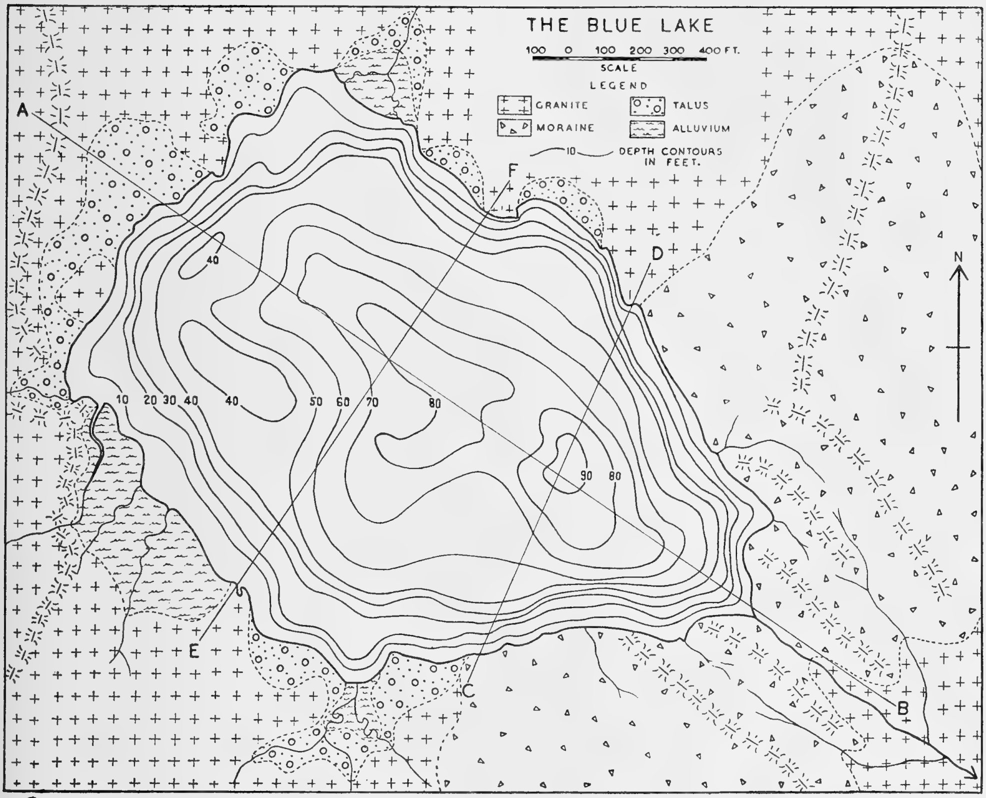

Fig. 2.

Furthermore, it will be noted that the 50, 60 and 70-foot contours to the north-east of the larger of the two elevations do not conform exactly with the adjacent shallower contours, and the spacing indicates a definite change in gradient between 40 and 50 feet. This change persists round the lake, indicating steep bottom-slopes near the shoreline, as illustrated at both sides of section A-B, and the southern side of section C-D. At places where granite *in situ* is not obscured by moraine, talus or alluvium, it is evident that the steep marginal slope beneath the water is a continuation of the profile above the shoreline. This feature is shown in sections C-D and E-F.

Modification of the shoreline by delta formation is confined to three small deltas, the largest of which is situated at the entrance of the main creek on the western side. Limited extension of the deltas beneath the water at these places is indicated by wider spacing of the contours up to 20 feet, and their conformity

with the delta shores. The occurrence of elevations and depressions on the floor of the lake, and the continuation beneath the surface of the steep profiles above the shoreline, would seem to indicate that no great quantity of silt has been deposited, as extensive silting would have filled depressions, buried elevations, and produced a more or less even sweep across the floor of the lake.

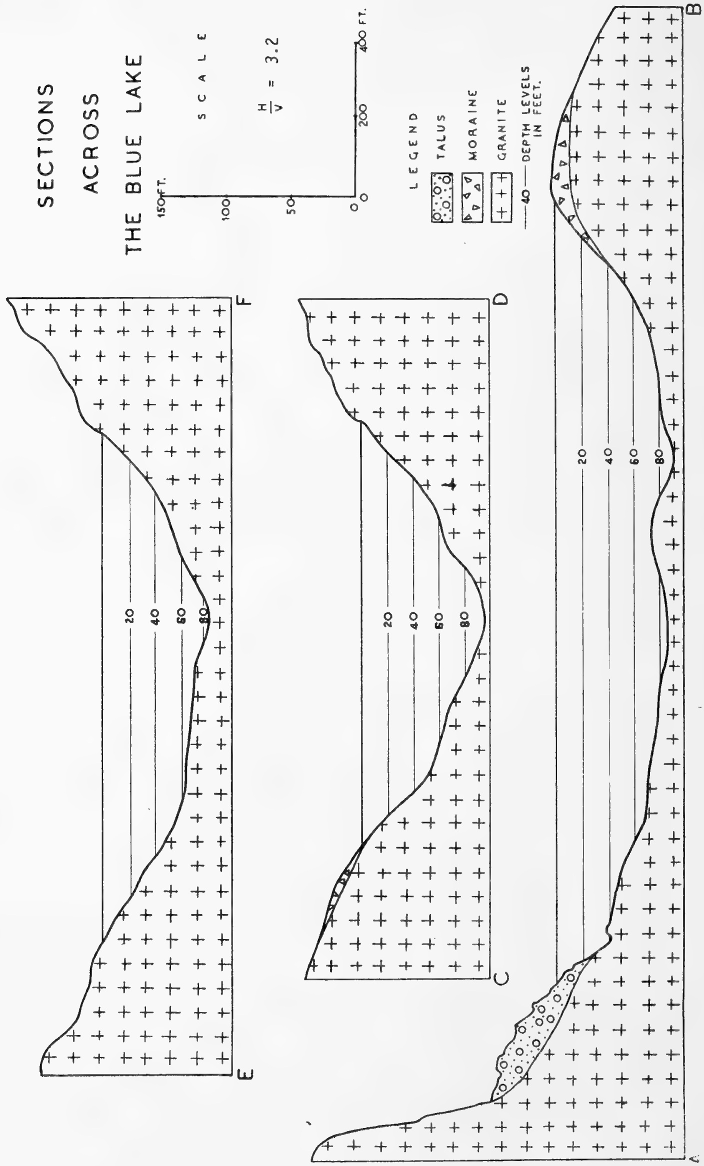

Fig. 3.

In 1901 David, Helms and Pittman described the terminal moraine dam of the Blue Lake as an extension of Helms Moraine, and suggested that the lake owed its origin chiefly to the moraine. In 1908, after David had taken some soundings of the lake, he concluded that it was " a true rock-hollowed basin ". The investigations recorded here provide quantitative data regarding the extent

to which the lake was over-deepened and moraine-dammed. Granite was found *in situ* in the bed of the exit-creek about 50 yards downstream from the lake and 15 feet below its surface. This means that the old valley-floor, where the lake now exists, was over-deepened by glacial action to the extent of at least 80 feet, as illustrated in section A-B, Fig. 3. It also means that the depth of morainic material between the lake level and the highest point of solid granite in the dam cannot be more than 15 feet, which represents the contribution of the moraine to the depth of the lake at the present time. The breach where the exit-creek passes through the moraine dam is about 35 feet deep. This does not mean that the water-level was ever 35 feet higher than it is now, as the moraine, at the dam, consists of five ridges running north-west and south-east parallel to the main trend of the valley, to the creek draining the lake, and to the direction of elongation of the lake. Also, the five ridges are situated at right angles to the general trend of the moraine as a whole (see Fig. 2). At first sight it may appear that the ridges resulted from the development of successive breaches occupied by the exit-stream. This could not be, as the exit-stream, having established itself in one breach, must have continued to deepen its channel, and would not abandon it to commence cutting another breach. Furthermore, the small valley-like features between the ridges contain miniature valley-divides, from which gullies run west back into the lake, and east away from it. Also, small valley-like features on the lake-side of the moraine extend beneath the existing level of the lake, which would not be the case if they were former breaches cut by the exit-stream.

In view of the foregoing observations, it appears that the parallel ridges running across the terminal moraine must have originated when the moraine was being built up—possibly due to the contribution of additional material from small medial moraines on the surface of the glacier. It follows that erosion of the exit-stream may not be responsible for the full depth of its present channel, but rather that when the stream originated it chose the deepest of the gaps between the ridges, and further deepened it into the breach which it now occupies. This possibility should be taken into consideration in speculations regarding former levels of the lake or the time, based on the depth of the breach, since the retreat of the glacier.

It may be concluded that the Blue Lake originated principally in the over-deepening of the valley floor, and that the terminal moraine, deposited at its lower end, played only a minor part in the damming of its waters.

The considerable size and depth of the Blue Lake probably resulted from excavation at the point of convergence of three valley glaciers. The largest of these gathered in the extensive amphitheatre which lies to the south-west of Mt. Twynam along the eastern side of the Main Divide, and forms the head of the main valley in which the Blue Lake is situated. Another glacier appears to have gathered in a smaller area to the east and north-east of Carruthers Peak, and moved east to Helms Moraine, where at least a portion of the ice spilled over the saddle at the western end of the moraine, and passed to the north-east, converging with the main glacier towards the south-eastern end of the Blue Lake. The third glacier accumulated to the north-north-east of the lake between Mt. Twynam and Little Twynam, and passed directly down the steep mountain side to meet the other two glaciers at a point between the centre and south-eastern end of the lake. Convergence towards the south-eastern end of the lake of the two smaller glaciers on either side of the main one may have been responsible for the greatest depth being there, and not at its broader north-western end beneath the hanging valley through which the main glacier entered, and where the greatest depth may be expected. The convergence of these glaciers must have resulted in medial-morainic material which could have produced the parallel ridges on the terminal moraine.

The Club Lake.

This lake, situated in a large cirque carved out of phyllite on the southern side of Carruthers Peak, is the smallest of the four lakes. It has a maximum width of 200 yards, and a surface area of only 3·6 acres (see Fig. 4). The lake is very shallow, with a maximum depth of between five and six feet. The shallow nature and bottom-shape indicate that it has been heavily silted. On its north-western and western sides, between the lake and the steep phyllite slopes of the cirque, there occur relatively large quantities of talus and alluvium, which appear to have accumulated where the lake has been filled. This would suggest that the lake has been reduced to perhaps one-half of its original size, and possibly to between one-quarter and one-sixth of its original depth by silting and talus-filling.

The waters of the lake are confined by a large moraine dam across its south-eastern side. The highest point at which phyllite was found *in situ* in the exit-creek was at a point about 175 yards below the dam, at a level of 110 feet below the surface of the lake. The slope down the lower side of the moraine is about 10°, whilst that of the phyllite surface below the moraine is 4°. If the phyllite surface retains this angle of slope beneath the moraine, it would rise to within about 55 feet of the lake level in the vicinity of the dam. It is impossible to estimate the exact depth of the lake before silting, but it is very unlikely that it exceeded 50 feet, which means that the lake probably owes its origin to the moraine dam rather than overdeepening of the valley.

The material forming the dam appears to be a terminal moraine deposited by ice which accumulated in the cirque at the final stages in the retreat of the valley glacier. Running across the surface of the moraine where it dams the lake are three parallel ridges trending north-west to south-east (Fig. 4), similar in character to those which occur on the terminal moraine at the Blue Lake. The tops of the ridges are almost 40 feet above the level of the lake and the exit-stream in the breach. On the lake side of the moraine the ridge and intervening valley-like features continue beneath the water and silt in the lake, as indicated by the bottom contours. From this, it is evident that the formation of the ridges on the moraine predated the filling of the lake with water, and later with silt; and it is possible that they originated from lines of medial morainic-material lying on the surface of the ice. The cirque in which the ice accumulated is large, and contains several small cirque-like features separated by spurs from which the medial morainic débris could have been derived. As in the case of the Blue Lake, it is considered that erosion by the exit-stream has not been responsible for the full depth of the breach in the moraine.

Lake Albina.

Lake Albina lies on the western fall of the Main Divide, in a deep valley running along the eastern side of the Townsend Range. The lake is situated mainly in Kosciusko gneiss, but its south-eastern extremity extends into phyllite which outcrops on the eastern side of the valley (see Fig. 4). The drainage is from south to north, and the lake is elongated in that direction, being almost divided into upper and lower halves by a constriction near its centre. The length of the lake is 650 yards, and its greatest width is about 200 yards. The total surface area is 16·2 acres.

The southern or upper half is comparatively shallow, possessing a maximum depth of about 11 feet. Towards the northern end of this half there occur on the bottom a central elevation and marginal depression which are believed to be a silt bank with channels on either side. This, together with the very shallow nature of its southern end, suggests that the upper half of the lake has been extensively silted.

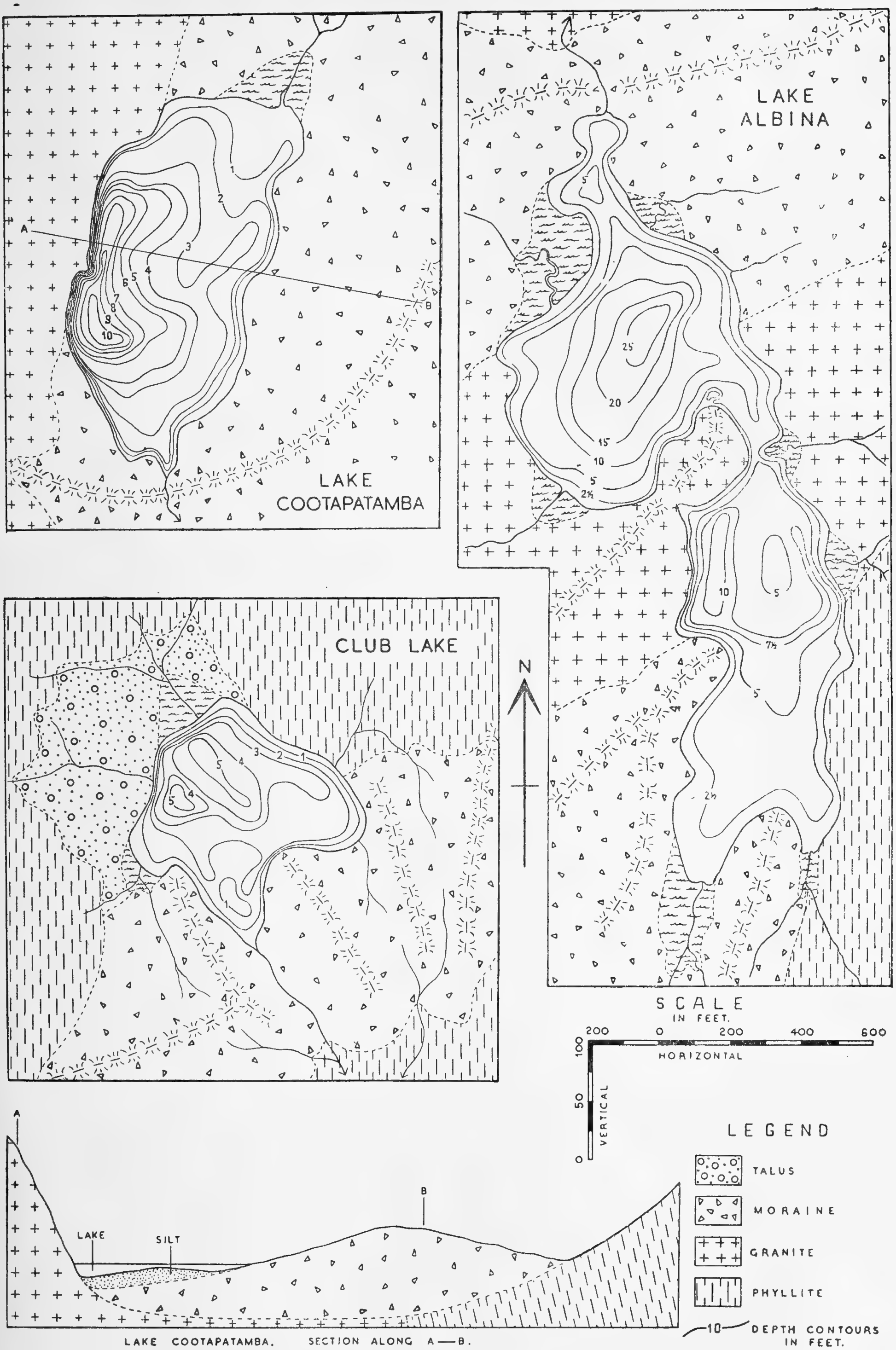
LAKE COOTAPATAMBA
LAKE ALBINA
CLUB LAKE
N
SCALE
IN FEET.
200 0 200 400 600
HORIZONTAL
100 50 0
VERTICAL
LEGEND
TALUS
MORAINE
GRANITE
PHYLLITE
10 DEPTH CONTOURS IN FEET.
A
B
LAKE
SILT
LAKE COOTAPATAMBA. SECTION ALONG A—B.

Fig. 4.

The lower or northern half of the lake is much deeper, reaching a maximum depth of 28 feet. The general bottom shape, and somewhat concave marginal slopes indicated by the depth-contours, suggest continuation beneath the water of the slopes above the shore-line, except on the north-western side where a delta has been built up by a creek draining a portion of the western side of the valley. Limited extension of the delta over the floor of the lake is shown by the depth contours. A small amount of sediment also appears to have been deposited on the eastern side where water enters from the upper half of the lake. These features indicate that extensive sedimentation has not occurred in the lower half of the lake.

The waters of Lake Albina are retained by a terminal moraine deposited across the valley. Gneiss outcrops in the exit-stream on the lower side of the moraine at about 130 feet below the lake level. The surface of the gneiss probably rises considerably beneath the moraine in the vicinity of the dam, but it appears highly improbable that it would rise above the level of the bottom of the lake. Thus it is believed that the terminal moraine is entirely responsible for the damming of the lake.

On the floor of the Albina Valley to the west of the lake, there occurs a great confusion of irregular moraine dumps, glaciated surfaces and ridges of gneiss, described by David, Helms and Pittman (1901). To the east of the lake there is but little morainic material on the valley side. Phyllite outcrops at the southern end of the upper half of the lake, and also along its eastern shore to the phyllite-gneiss junction, after which gneiss outcrops until the terminal moraine is reached. A prominent ridge of gneiss trending south-west and north-east rises above the morainic débris, and runs down the western side of the valley across the floor to the centre of the lake, where it forms the constriction between the two halves. This ridge also divides the western side of the valley into two areas, one of which drains into the upper half, and the other into the lower half of the lake.

The direction of ice movement during the glaciation of the Albina Valley is somewhat obscure, as discussed by David, Helms and Pittman ; but the north-easterly trend of grooves on the ice-smoothed pavements, and the presence of the ridge described above, suggest to the present writer that the western side of the valley was occupied by two small valley glaciers which passed obliquely across the floor in a north-easterly direction, before uniting and turning north to follow the general trend of the valley. The two glaciers evidently built up the terminal moraine which dams the lake, and later, after a short, rapid retreat, which left the area of the lake comparatively free from débris, continued to dump irregular masses of moraine on the floor and western side of the valley.

Thus it is concluded that Lake Albina originated during the closing stages of valley glaciation, after the retreat of ice from the eastern side of the valley floor, where water accumulated between the terminal moraine and the confused morainic dumps later deposited on the western side.

Lake Cootapatamba.

Lake Cootapatamba occurs on the western side of the Main Divide in a glaciated valley lying immediately to the south-east of Mt. Kosciusko. It is situated in Kosciusko gneiss, close to the boundary of phyllite occupying the eastern side of the valley. The lake is roughly oval in shape, 300 yards long and 150 yards wide, with a surface area of 8·4 acres (see Fig. 4). The deepest sounding obtained was 10 feet 6 inches, indicating a maximum depth of perhaps 11 feet. An approximate depth of 17 feet was recorded by David, Helms and Pittman (1901). The depth contours show very steep marginal bottom-slopes along the western side, where the deepest part of the lake occurs ; but shallow conditions with gentle slopes prevail over the remainder of the lake (see section

A-B, Fig. 4). A delta has been built up at the northern end where the main creek enters, and the extension of delta material to the centre of the lake is indicated by depth-contours. This and shallow-water conditions at the southern end of the lake suggest extensive silting.

The lake is bounded at its lower end by a terminal moraine described in detail by David, Helms and Pittman. It is 70 to 80 feet deep in the vicinity of the exit-creek, from which it may be concluded that the lake originated from moraine-damming rather than overdeepening of the U-shaped valley (see section A-B)—even if the original depth of the lake were as much as five times its present depth.

The eastern end of the terminal moraine merges into a lateral moraine lying along the eastern side of the lake, and occupying a central position on the valley floor. The material of the lateral moraine forms the eastern shore of the lake, but gneiss occurs *in situ* along the western shore at the base of steep slopes rising to a spur from Mt. Kosciusko. It is probable that the present bottom-shape of the lake, although heavily silted, is similar in a general way to the original shape before silting, as the steep marginal slopes on the western side represent an extension beneath the water of the steep valley side above the shore-line. The gentle slopes on the eastern side conform to the gently-dipping surface of the débris flanking the lateral moraine, as illustrated in section A-B, Fig. 4. It follows that the water of the lake must have accumulated between the lateral moraine and the western side of the valley above the terminal moraine, in a small space left after the retreat of the glacier ice.

Silting of the Lakes.

Sediment deposited in the Blue Lake has been sufficient only to build up deltas which are relatively small compared with the size of the lake. Material carried into Lake Albina has been almost sufficient to fill the upper half, but not the lower half of the lake. Lake Cootapatamba has received a considerable quantity of silt, but has not been filled ; and the Club Lake, although practically filled, has not yet reached the final swampy stage characteristic of older, completely-silted lakes occurring at somewhat lower altitudes.

Dams constructed in valleys, even near their headwaters, rapidly fill with silt unless provision is made for flushing. In some cases small dams, comparable in size with the alpine lakes at Kosciusko, have been filled in periods of from 100 to 200 years, and under normal conditions a life of no more than several hundred years can be expected of dams from which water escapes solely by overflow.

The alpine lakes are at least 10,000 years old (David, 1908 ; Browne, 1945) but relatively little sediment has been introduced. A possible explanation of the small quantities of sediment transported by streams from areas above the lakes is the influence of specialised climatic conditions on growth of vegetation and soil-formation above 5,000 feet (Browne, Dulhunty and Maze, 1944). Winter snows cover the ground from seven to nine months of the year, and during the brief summer period there is a tremendous growth of snow grass and herbage on the permanently saturated soil. Each summer after the thaw more grass grows on top of last year's dead, but preserved, growth, with the result that from six to eighteen inches of moor peat forms a protective blanket on the slopes and hillsides. Fibrous peat beds are developed in flat, swampy areas, and peaty soils with vegetation dams are built up on hillsides, holding up drainage and producing conditions which are the reverse of soil erosion. Sandy soil that under normal conditions of erosion would be washed from the hillsides is caught up and held in the blanket of grass. Water, too, is held up, forced to run at random over the grass, and small streams flow over the surface of the turf. The streams meander, pushed about by the body of growth, and where they have succeeded in maintaining channels, they are confined to very narrow beds by the tough

grasses, so that a minimum amount of soil reaches the lakes. Very often the creeks run underground for considerable distances. This is caused by the thick growth meeting and intertwining overhead, sand being caught and held, and new grasses taking root until solid turf is formed over the streams. Exposed surfaces of granite and phyllite are subjected to disintegration by frost action, but the products of erosion are largely retained on the grassy hillsides and valley floors, very little passing downstream into the lakes.

Phyllite, weathering more rapidly than granite, produces greater quantities of silt, and silting of the lakes is influenced by its presence in their watersheds. However, the rate of silting is not directly proportional to the area of phyllite, as the area of phyllite above the Blue Lake is much greater than that above the Club Lake, yet the latter is practically filled, while the Blue Lake is only slightly silted. This can be explained by the fact that the Club Lake is surrounded by phyllite which extends to the shore-line, but at the Blue Lake the area of phyllite is some distance away; and the products of erosion during the post-glacial period have been retained on the hillsides, in cirques and swampy areas before reaching the lake. It follows that the influence on rate of silting depends more on the proximity of the phyllite to the lakes than the area which it occupies.

Thus it is concluded that abnormal conditions of vegetation and soil formation existing on the undissected, glaciated surface of the plateau have been responsible for the survival of the alpine lakes throughout the post-glacial period.

Acknowledgment.

It is wished to acknowledge valuable discussion during the preparation of this paper with Dr. W. R. Browne. The author is also grateful to Dr. Browne for an introduction to the glaciology of the Kosciusko district.

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NOMOGRAMS FOR SOME ASTRONOMICAL COMPUTATIONS.

By H. W. Wood, M.Sc.

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Nomographic solutions, which are often used for equations which have to be solved approximately many times have the advantage, apart from avoiding some of the trouble that must be taken when accuracy is required, of freeing the solver from the necessity for reference to tables and the like. Even when an exact result is required an approximate one may be useful as a starting point in an iterative process. Some solutions of this kind are suggested in the notes which follow.

Kepler's Equation.

$$M-E+e \sin E=0$$

connecting mean anomaly (M), eccentricity (e) and eccentric anomaly (E) in planetary motion may, by putting $N=E-M$, be written

$$N-e \sin (M+N)=0 \qquad (1)$$

which may be expressed as a determinant

$$\begin{vmatrix} 0 & N & 1 \\ \sin (M+N) & 0 & 1 \\ 1 & -e & 0 \end{vmatrix}=0$$

If the elements of each row are regarded as the homogeneous cartesian coordinates of a point in a plane, this equation expresses the condition for their collinearity. When the linear transformation

$$[x'_s]=[a_{st}][x_s]$$

is applied to this, it becomes

$$\begin{vmatrix} a_{12}N+a_{13} & a_{22}N+a_{23} & a_{32}N+a_{33} \\ a_{11} \sin (M+N)+a_{13} & a_{21} \sin (M+N)+a_{23} & a_{31} \sin (M+N)+a_{33} \\ a_{11}-a_{12}e & a_{21}-a_{22}e & a_{31}-a_{32}e \end{vmatrix}=0$$

Dividing through by the last element of each row expresses this in ordinary cartesian coordinates. The placing of four points of the nomogram, for example the terminal points of N and e, to suit convenience gives eight equations determining eight of the elements of $[a_{st}]$ in terms of the remaining one. The three curves

$$x=\frac{a_{12}N+a_{13}}{a_{32}N+a_{33}}, \quad y=\frac{a_{22}N+a_{23}}{a_{32}N+a_{33}}; \quad \text{etc.}$$

may be drawn and graduated with the values of the respective variables N, e and M+N. Figure 1 covers the range of values for $e<0\cdot2$. By rotating a thread (or better a straight line ruled on glass or celluloid) about the point corresponding to the value of e, it is easy to find the alignment which gives

M+N (from nomogram)=M (calculated)+N (from nomogram).

From a diagram of this kind ten inches by ten inches the value of N can be read to a hundredth of a degree. The method given by S. Brodetsky (1938) and W. C. Rand (1942) has the advantage of greater directness, but this solution of Kepler's equation is somewhat easier to draw and accuracy is easier to attain with it. The flexibility of nomographic solutions lies in the possibility of

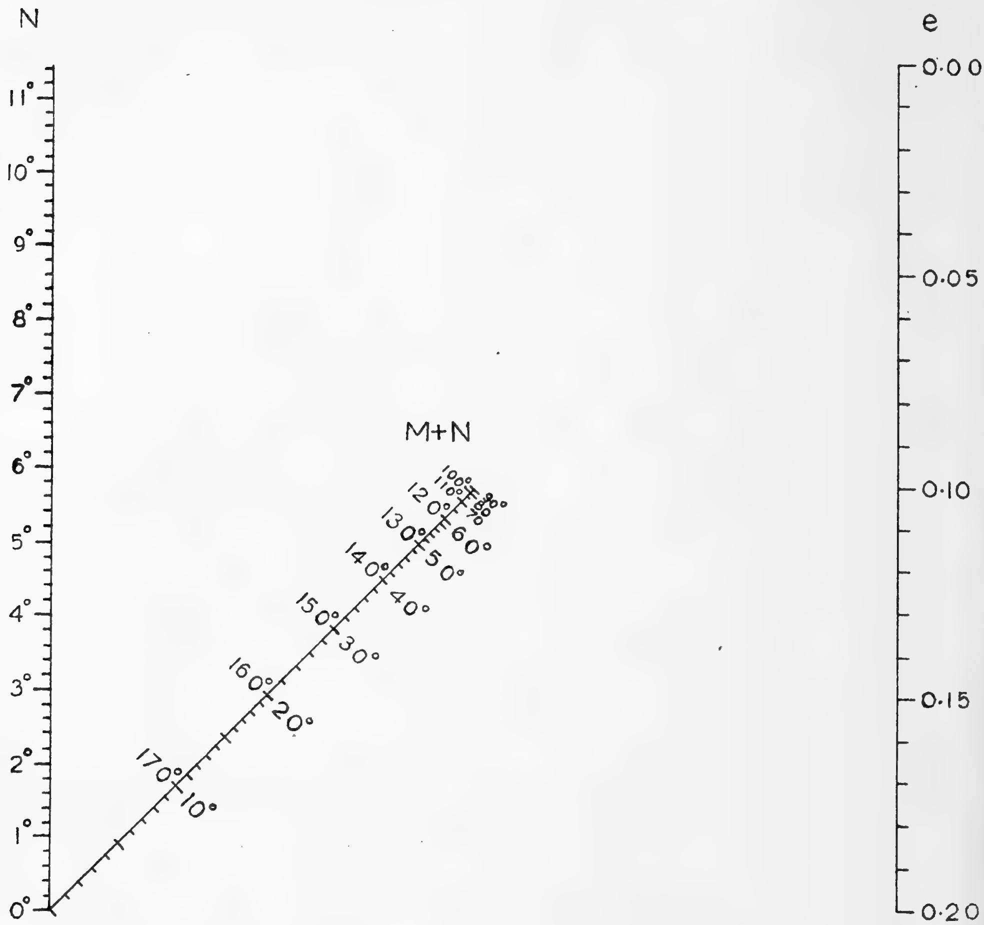

Fig. 1.

expanding the scale indefinitely by drawing a series of diagrams to cover the range of values. A set of drawings of this kind can be useful as a ready source of approximate solutions of the equation for double star ephemerides, for commencing iterative processes or for teaching purposes.

In the iterative process for correcting the preliminary value of E

$$\triangle E = \frac{1}{1 - e \cos E} \triangle M = L \triangle M$$

a similar nomogram to the above will give the coefficient of $\triangle M$ with sufficient accuracy, that is, the nomogram for

$$\left(1 - \frac{1}{L}\right) - e \cos E = 0.$$

A similar diagram graduated for the equation

$$R=\frac{\sin A}{\sin a}$$

may be used for solving the sine rule equations of spherical triangles. For example, in some navigation tables the observer has facilities for computing the altitude from hour angle and declination and is left to find the azimuth of the observed object either graphically or by separate computation. This may be done with such a nomogram since

$$\frac{\sin t}{\sin z}=Q=\frac{\sin A}{\sin (90°-\delta)}$$

(t is hour angle, z zenith distance, A azimuth, and δ declination) and when necessary the ambiguity in A may be resolved since the zenith distance when the object is on the prime vertical is given by

$$\sin (90°-z)=\frac{\sin \delta}{\sin \varphi}$$

which may be provided for by a graduation for z on the central scale.

Refraction, using the Poulkovo Refraction Tables (1870 and 1930) is given by

$$r''=\mu \tan z(BT)^{A}\gamma^{\lambda}\sigma^{\iota}$$

where μ, A, λ and σ are functions of the zenith distance, B depends on the reading of the barometer, T on the temperature of the (mercurial) barometer, γ on the atmospheric temperature, ι on the time of the year, and r″ is the refraction in seconds of arc. Neglecting factors whose influences remain under one per cent. (i.e. $\log < 0 \cdot 004$)

$$r''=\mu \tan z\gamma B\gamma^{\lambda-1}$$

$$\text{Putting } \log S=\log \gamma+\log B+\log \gamma^{\lambda-1}$$

$$=a+b+c$$

$$r'=R'_0 S.$$

(R'_0 is the mean refraction in minutes of arc.)

The values (in units of the third decimal place) of a, b and c, for the values of pressure, temperature, and temperature and altitude may be taken from Table I. These are added to give S, which with the observed altitude (H) of the heavenly body will give the required value of refraction to be subtracted from H to give true altitude (Fig. 2).

TABLE I.

Table for *a*.				Table for *b*.			
Temp. ° F.	*a*.	Temp. ° F.	*a*.	Pres. Ins.	*b*.	Pres. Ins.	*b*.
20	+25	60	−10	22·5	−119	27·0	−40
25	+21	65	−14	23·0	−109	27·5	−32
30	+16	70	−18	23·5	−100	28·0	−24
35	+12	75	−22	24·0	−91	28·5	−16
40	+8	80	−26	24·5	−82	29·0	−9
45	+3	85	−30	25·0	−73	29·5	−1
50	−1	90	−34	25·5	−65	30·0	+6
55	−5	95	−38	26·0	−56	30·5	+13
				26·5	−48	31·0	+20

TABLE I—*Continued.*
Table for c.

H. \ Temp.	10°	9°	8°	7°	6°	5°	4°	3°
20	+1	+1	+1	+2	+2	+3	+4	+6
25	+1	+1	+1	+2	+2	+3	+3	+5
30	+1	+1	+1	+1	+2	+2	+3	+4
35	0	+1	+1	+1	+1	+1	+2	+3
40	0	0	0	+1	+1	+1	+1	+2
45	0	0	0	0	0	0	0	+1
50	0	0	0	0	0	0	0	0
55	0	0	0	0	0	−1	−1	−1
60	0	0	−1	−1	−1	−1	−2	−2
65	−1	−1	−1	−1	−1	−2	−2	−3
70	−1	−1	−1	−1	−2	−2	−3	−4
75	−1	−1	−1	−2	−2	−3	−4	−5
80	−1	−1	−2	−2	−2	−3	−4	−6
85	−1	−1	−2	−2	−3	−4	−5	−7
90	−1	−2	−2	−3	−3	−4	−6	−8
95	−2	−2	−2	−3	−4	−5	−6	−9

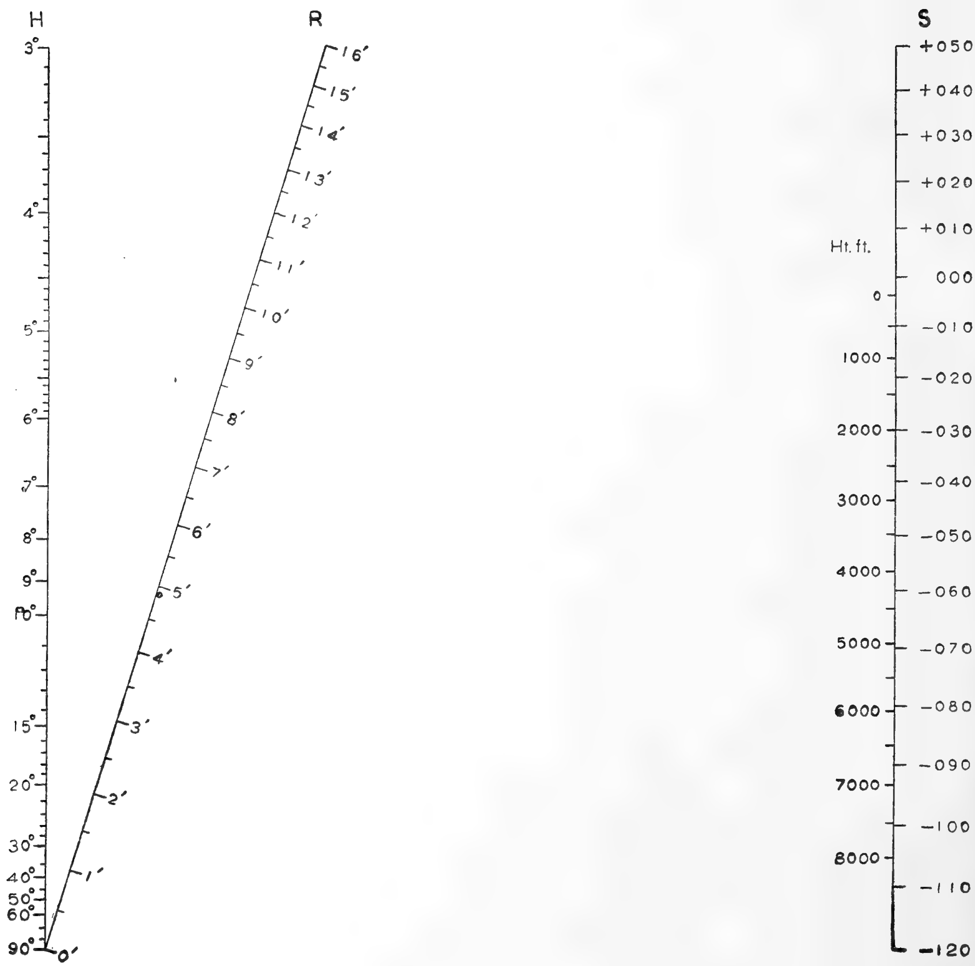

Fig. 2.

The values of S at various heights above sea level corresponding to a mean atmosphere (Humphreys, 1940) having been calculated, the right-hand scale has been graduated in height above sea level and the refraction may be found, if the pressure and temperature are not known, by aligning the corresponding point on this side with the altitude on the left-hand scale. In accuracy and convenience this method is satisfactory when compared with the usual tables given for navigational purposes.

Spherical triangles may be solved by repeated use of the equation

$$\tan Y - \tan X \sec Z = 0.$$

Write this

$$U - VW = 0 \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

which could be solved in the same way as equation (1) or by writing in the form

$$\log U - \log V - \log W = 0$$

either of which becomes awkward for very large or small values of the variables.

However, the left-hand member of equation (2) is a factor of

$$\begin{vmatrix} V^2 & V & 1 \\ U & 0 & 1 \\ W^2 & -W & 1 \end{vmatrix} \quad \dots\dots\dots\dots\dots\dots (3)$$

so that solutions to the equation may be obtained by taking the elements of each row as cartesian coordinates and drawing and graduating the parabola corresponding to V and W and the straight line (x axis) for U. The effect of the factor $(V+W)$ in (3) is removed by always taking the values of V and W from the scale along the parabola on opposite sides of its axis.

On applying the transformation

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}$$

to (3) we obtain

$$\begin{vmatrix} V^2 & V & 1+V^2 \\ U & O & 1+U \\ W^2 & -W & 1+W^2 \end{vmatrix}$$

which projects the parabola into a circle.

Figure 3 is drawn by putting $U=\tan Y$, $V=\tan X$ and $W=\sec Z$. This nomogram may be applied to the solution of the usual " logarithmic " formulæ for obtaining azimuth and zenith distance from hour angle and declination

$$\tan N = \frac{\tan \delta}{\cos t}, \quad \frac{\tan A}{\cos N} = \tan R = \frac{\tan t}{\cos\{90^\circ - (\varphi - N)\}}, \quad \tan z = \frac{\tan(\varphi - N)}{\cos A}$$

(t, δ, z, A as above, φ latitude, and N and R are auxiliaries).

If $z=90^\circ$, that is, at rising or setting,

$$\tan(90^\circ - \varphi) = \frac{-\tan \delta}{\cos t}, \quad \tan t = \frac{-\tan A}{\cos(90^\circ - \varphi)}$$

so that the same nomogram will give the hour angle and azimuth of rising or setting.

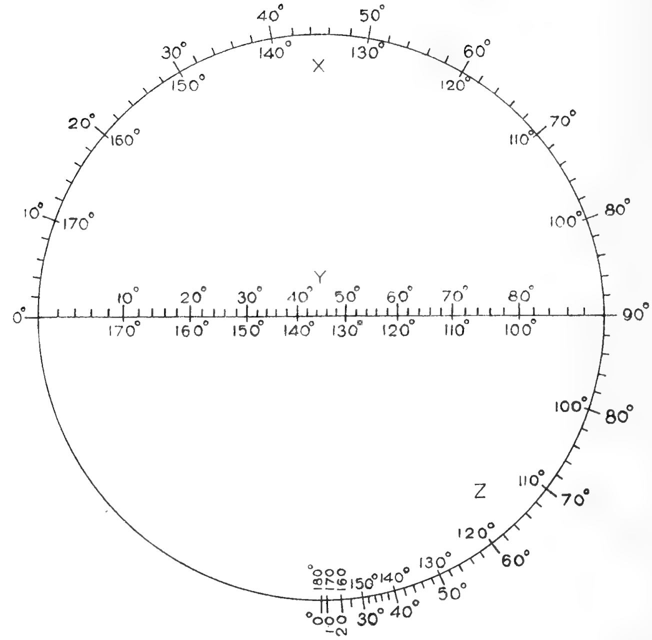

Fig. 3.

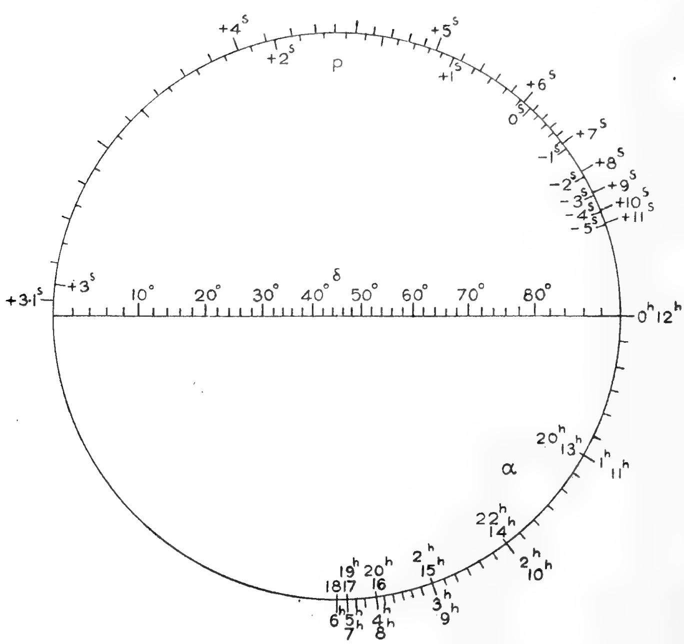

Fig. 4.

Frequently substitution into an existing nomogram will facilitate the solution. For example, the formula for precession in right ascension

$$p = m + n \sin\alpha \tan\delta$$

may be written

$$\tan\delta - \frac{p-m}{n} \operatorname{cosec}\alpha = 0.$$

Now if we put

$$\frac{p-m}{n} = \tan X, \quad \tan\delta = \tan Y, \quad \operatorname{cosec}\alpha = \sec Z$$

and solve these equations for the values of p, δ and α we wish to have on the nomogram and regraduate Fig. 3 at the places indicated by the solutions, the alignments will give the solutions of the equation for precession in right ascension. This is done in Fig. 4. Obviously if the precession in right ascension for a certain number of years of a series of objects was wanted the same nomogram could be regraduated to give the result without multiplication.

Similarly the solution of the equation

$$\tan \tfrac{1}{2}E = \left(\frac{1-e}{1+e}\right)^{\frac{1}{2}} \tan \tfrac{1}{2}v$$

connecting the eccentric anomaly E with the true anomaly v and eccentricity e can be obtained by regraduating the nomogram for

$$\tan Y - \tan X \sec Z = 0$$

at the points indicated by

$$\tan \tfrac{1}{2}E = \tan X, \quad \left(\frac{1+e}{1-e}\right)^{\frac{1}{2}} = \sec Z, \quad \tan \tfrac{1}{2}v = \tan Y.$$

The solutions obtained in this way might be useful for computing double star ephemerides.

Although the drawing and lettering on plain paper of diagrams like those prepared for reproduction here represents some trouble, they can be quickly done on squared paper and are somewhat more useful.

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SOME DIFFICULTIES IN THE LEWIS AND CALVIN THEORY OF LIGHT ABSORPTION.

By D. P. Craig.

Manuscript received, October 15, 1945. Read, November 7, 1945.

Introductory.

The theory of the relation between light absorption and chemical constitution of organic molecules proposed by Lewis and Calvin (1939) can be applied to molecules much more complex than those for which approximate quantum mechanical and group theoretical methods are available (e.g. Sklar, 1937; Forster, 1939; Mulliken, 1939). It has generally been taken, and indeed is implied by the authors themselves (Lewis and Calvin, 1939; Lewis, 1945) that the theory is compatible with the more exact work and that it applies to complex structures principles proved correct in simple cases. However important modifications to the theory are necessary in order to bring it into line with the quantum mechanical analysis, and in the following, the treatment of the benzene and acridine molecules and of some simple derivatives, will be considered from this point of view.

Benzene.

The Lewis and Calvin theory associates the process of light absorption with the excitation of a quasi-classical oscillation of electric charge within the molecule. In ethylene, for example, the fundamental process is taken to be the excitation of the $CH_2{=}CH_2$ structure to give the structures $\overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2$ and $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H_2$, in which an electron pair oscillates towards the carbon atoms at a frequency dependent on a classical restoring force constant for the system. The absorption spectrum then shows a band at and about this frequency. In benzene it is supposed that the longest wave-length band (2,600 Å.) is due to the excitation of charge oscillations between structures like

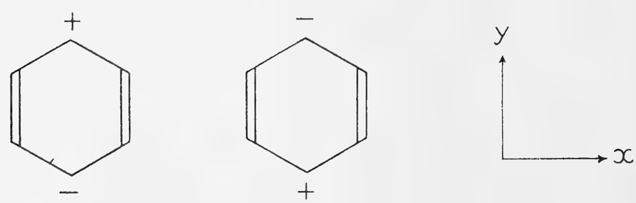
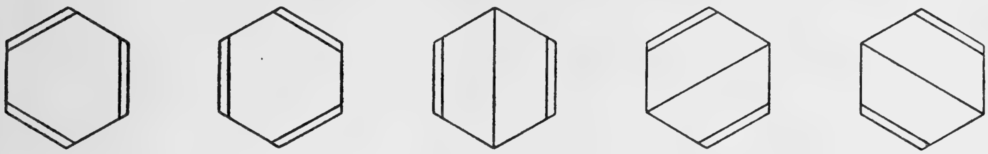


Fig. 1.

in which there is an oscillation of charge towards these extremes. The ground state is taken as a resonance hybrid of uncharged Kekulé and Dewar structures



A B C D E

Fig. 2.

and the excited or upper state involves charged structures having axial symmetry (Fig. 1). The weakness of the 2,600 Å. absorption is taken as evidence that a high resonance energy does not imply intense light absorption, and that the Kekulé structures which are responsible for most of the resonance energy are not important in the absorption process. The high symmetry of the benzene molecule enables some deductions to be made on symmetry grounds alone from the foregoing proposed mechanism. It can then be seen that the mechanism will not account for the observed features of the absorption.

A structure having axial symmetry, such as the ionic structures of Fig. 1,[1] can be regarded as a perturbed state of the totally symmetric benzene molecule, and can therefore be expanded in terms of the irreducible representations of the group of operations of symmetry D_{6h}; such structures transform like

$$A_{1g}+E_{2g}+B_{1u}+E_{1u}$$

A transition between two states of given symmetries is allowed if the direct product of their irreducible representations with that of any one of the cartesian coordinates contains the totally symmetric representation A_{1g}[2]; we can see that the proposed transition would be an allowed one by considering the direct product:

$$A_{1g}E_{1u}E_{1u}=A_{1g}+E_{2g}+A_{2g}$$

where the ground state belongs to the totally symmetric A_{1g} and the coordinate in the plane of the ring transforms like the degenerate E_{1u} ($=E_u^-$). The direct product contains A_{1g}, the transition moment is therefore not zero, and the transition is an allowed one. Further, the transition moment will be at right angles to the axis of the ionic structure (not along the axis, as required by the Lewis and Calvin theory) since the moment must be symmetrical under the operations of the perturbed state; the moment in the y direction (Fig. 1) must be zero, since the direct product $A_{1g}yB_{2u}$ is antisymmetrical under C'_2. However, $A_{1g}xB_{2u}$ is symmetrical under C'_2 and the non-vanishing transition moment is in the x direction. Thus if the Lewis and Calvin transition were the one

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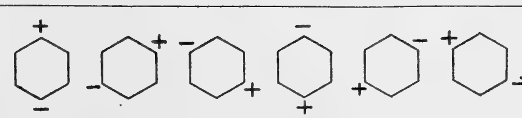
[1] Symmetry of structures of Fig. 1:



1 2 3 4 5 6

Reducible representation:	E	C_2	$2C_3$	$2C_6$	$3C'_2$	$3C''_2$	i	h	$2S_6$	$2S_3$	$3S''_2$	$3S'_2$
	6	0	0	0	6	0	0	6	0	0	0	6

Irreducible set: $A_{1g}+E_{2g}+B_{1u}+E_{1u}$.

[2] This is the requirement, on symmetry grounds, that $\int\psi_1 x\psi_2 d\tau\neq 0$ where ψ_1 and ψ_2 are electronic wave functions for the ground and excited states.

responsible for the 2,600 Å. band, the absorption should be of large intensity (being allowed) and the moment should be at right angles to the axis of charge separation.

However, the measured 2,600 Å. band is very weak, and the reason for this is apparent in the theoretical treatment of Sklar (1937), in which it is shown that the long-wave absorption of benzene can be accounted for very well by the bond eigenfunctions approximation using Kekulé and Dewar structures as the basic set, and taking no account of ionic structures. The excited level then transforms not like E_u^- but like B_{2u} and the direct product $A_{1g}E_u^-B_{2u}=E_{2g}$ now does not contain the totally symmetrical A_{1g}, and the transition is therefore a forbidden one. That the band appears at all is the result of the occurrence of nuclear vibrations of symmetry E_{2g}, which perturb the ground state and make the transition permitted in second approximation:

$$A_{1g}E_{2g}E_{1u}B_{2u}=A_{1g}+E_{2g}+A_{2g}.$$

The vibrational fine structure of the absorption and its temperature dependence support the proposed mechanism (Sklar, 1937).

It is clear then that the Lewis and Calvin mechanism for absorption in benzene leads to incorrect expectations both with regard to intensity and to the importance of ionic structures in the first excited state. Perhaps the most significant feature of the quantum mechanical treatment is that ionic forms of the kind employed by Lewis are not important in the normal and first excited states; in fact, their inclusion either in the ortho or para form would give the absorption the characteristics of an allowed transition.

Calculations by Förster (1939) for naphthalene, anthracene, fulvene and naphthacene based only on Kekulé-like structures confirm that for these molecules also ionic structures need not be considered in accounting for the long wave absorption bands; it seems reasonable to suppose that the same would apply to more complex condensed ring homonuclear molecules.

Substituted Benzenes.

A single substitution in benzene causes a departure from sixfold symmetry. The extent of this perturbation is dependent on the nature of the substituent, being larger for $-NH_2$ and $-NO_2$ than for $-CH_3$ and $-Cl$, and being rather small in the case of a predominantly inductive interaction such as that of $-\overset{\oplus}{N}H_3$.

An oscillation of charge between the structures

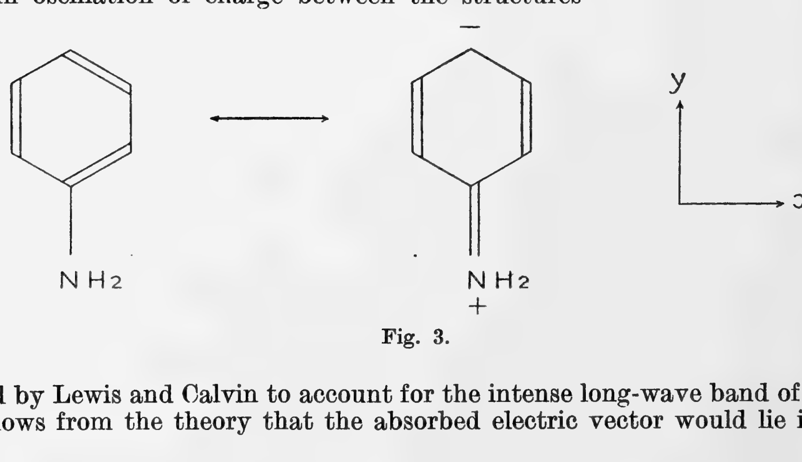


Fig. 3.

is held by Lewis and Calvin to account for the intense long-wave band of aniline. It follows from the theory that the absorbed electric vector would lie in the y

direction—i.e. in the direction of greatest extension of the molecule. The absorption of aniline, then, reflects the formation of a "new resonance path" in the molecule, and the fact that the anilinium ion reverts to a benzene-like absorption is the result of the closing of this resonance path by making impossible the double bonded structures like (2) above.

There can be little doubt that ionic structures are important in accounting for the properties of aniline (for example, the reduced basic dissociation constant as compared with methylamine) and in general the Lewis and Calvin theory seems much more satisfactory for heteronuclear systems than for homonuclear ones. It is clearly not the case, however, that the transition moment is in the y direction, since the argument already used for the axially symmetric structures of benzene shows that it is the x moment which is non-vanishing under the operations of C_{2v}.

The perturbation of the sixfold benzene symmetry results both in making the $A_{1g}-B_{2u}$ transition partially permitted and thus increasing its intensity according to the strength of the perturbation, and also in lowering the energy levels involved and thus increasing the wave-length of the absorption maximum. In general, in the mono-substituted benzenes, large perturbations are associated with greatly enhanced intensities and large wave-length shifts of the $A_{1g}-B_{2u}$ band.

The basis for the Lewis and Calvin theory is to be found in the fact that ionic structures, where they occur, are more important in the excited levels of a molecule than they are in the ground level; they reduce the energy difference between the two states as compared with a molecule in which similar ionic structures are unimportant. In aniline, for example, the ground state is stabilised by 6–9 Kg. cals. per mole as compared with benzene (thermal measurements and dissociation constant evidence), whereas in the upper state the ionic structures cause a lowering of about 20–23 Kg. cals. from the benzene value (absorption spectrum). It cannot of course be said that the ionic structures are responsible for the absorption, since in most cases the transition is between states to which the contributors are predominantly covalent; what can be said, however, in the case of highly stabilised structures such as benzene, pyridine, naphthalene, quinoline, anthracene, acridine, etc., is that any change in the molecule (e.g. substitution or ionisation) which increases the importance of ionic structures in the ground state will decrease the separation of the ground and first excited levels of the molecule, and will thereby increase the wave-length of the corresponding absorption maximum. Conversely, a decrease in contribution by ionic structures will have the opposite effect. Thus while the ionisation of acridine enhances ionic contributors such as

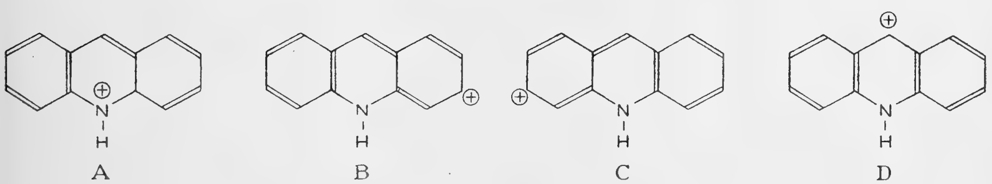


Fig. 4.

and has a bathochromic effect, the ionisation of aniline suppresses certain ionic structures (i.e. those giving the nitrogen atom a formal positive charge) and shortens the wave-length of the absorption maximum.

Directional Effects in Acridine.

Lewis's rules for the prediction of the long wave-length band of dyes from structure do not give a good account of acridine dyes of the general structure (double bonds omitted)

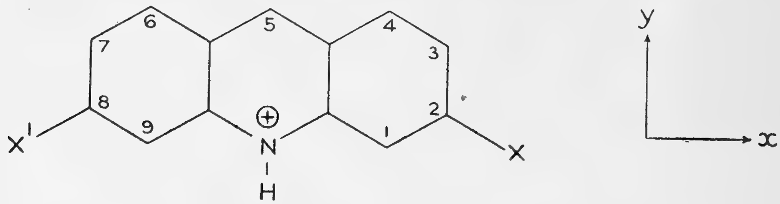


Fig. 5.

in which X and X′ are substituted amino groups. Lewis accordingly suggested (Lewis, 1945) that the observed long wave band for these dyes corresponds with an oscillation of charge in the y direction of the molecules, i.e., along the short axis of the structure. Although this cannot be ruled out directly from symmetry considerations, it appears to be unlikely in the light of investigations on the monoamino- and some diamino-acridines (Craig and Short, 1945) in which it is shown that substitution of an amino group in the 5– position has a negligible effect on the long wave band, whereas substitution in the 2– position, and, even more, disubstitution in the 2– and 8– positions has a marked bathochromic effect. Thus the absorption maximum is sensitive to extensions of the electronic configuration in the x direction and insensitive to them in the y direction ; there are, of course, changes caused in deeper energy levels by these latter extensions.

Sufficient symmetry is possessed by some of these substances to make it seem almost certain that the x vibration (in Lewis's terminology) is that responsible for the long wave-length band. Forster (1939) has shown that the first transition in anthracene can be well accounted for using only the four Kekulé-like structures

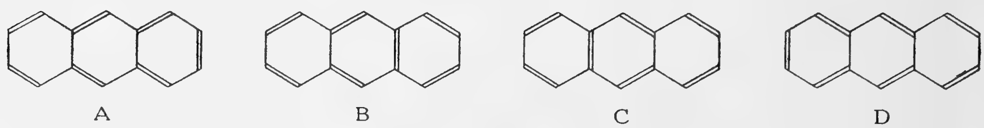


Fig. 6.

Using such structures, the two levels between which the transition occurs are of symmetries A_{1g} and B_{3u}. The electric vector which is active is that in the x direction : $A_{1g}xB_{3u}=A_{1g}B_{3u}B_{3u}=A_{1g}$, and the y direction is inactive. This has been confirmed experimentally by Scheibe (1938). Acridine has an absorption spectrum which is almost identical with that of anthracene in the ultra-violet, so that although its nuclear symmetry is lower (C_{2v}) than that of anthracene, the electronic symmetry and energy level of spacing of both molecules must be much the same. We may therefore assign the long wave-length band of acridine to an x vibration.

The monoaminoacridines all have lower electronic symmetry than D_{2h}. 5-Aminoacridine has the properties of C_{2v}, and the long wave absorption band can be shown to be due to a transition between states A_1 and B_1 ; both the x and y electric vectors are active in inducing this transition. The other amino-acridines are of still lower symmetry and no immediate conclusions can be drawn on symmetry grounds as to the directional properties. However, one method

of procedure is still possible. Suppose 2 : 8 diaminoacridine is under investigation : we can construct a hypothetical polyamino-compound of high symmetry which is expected to be spectrographically similar to the actual compound, determine the direction of the absorbed electric vector, and then, by analogy, deduce the direction for the known compound.

Considering, then, the structure

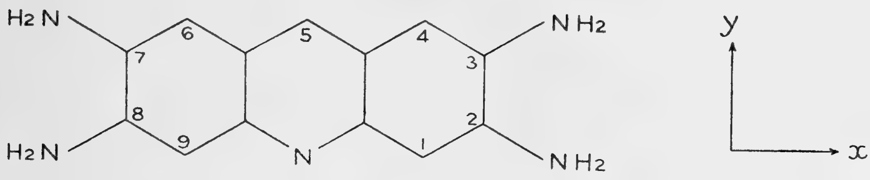


Fig. 7.

and assuming that, as in acridine, the ring —N= behaves as —CH=, it can be seen that this molecule has symmetry D_{2h} and that its first absorption will involve states A_{1g} and B_{3u}. As already seen, such a transition is permitted only for the x electric vector. It is clear that in the known compounds 2 : 7- and 2 : 8-diaminoacridine the absorption will also be predominantly in the x direction, with the difference that the same transition will also be allowed to a small extent (dependent on the perturbation from twofold symmetry about the x axis) for the y electric vector.

From this point of view, the effect of ionisation of the ring nitrogen atom is to increase the dissymmetry of the structure about the x axis, and hence to increase the transition probability for the y direction of the electric vector. Thus in acridine, for example, the effect of ionisation, apart from the decrease in separation of the energy levels, is expected to be an increase in the total transition probability for the long wave-length band. Preliminary estimates of transition probability from the areas of the absorption bands of acridine fully confirm this expectation.

Summary.

Some features of the Lewis and Calvin theory of the light absorption of organic structures are compared with the group theoretical treatment of Sklar and others. A modified rule of colour is suggested to cover cases of substitution and ionisation in ring systems. Some deductions are made to show that the long wave-length absorption of aminoacridines is excited by light whose electric vector is parallel to the long axis of the molecule.

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PROPERTIES OF FILMS OF NITROGEN ON TUNGSTEN.

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The contact potential difference method of studying the properties of adsorbed films (Bosworth and Rideal, 1937 ; Bosworth, 1945) exhibits its versatility to no better effect than when treating the subject of the properties of nitrogen on tungsten films. These films evaporate at such a low temperature that the system is completely inaccessible to the thermionic method, which, in the hands of Kingdon (1924), had yielded some information, albeit a little misleadingly, concerning the properties of oxygen on tungsten films. Some of the properties of the nitrogen on tungsten films have been recorded by Van Cleave (1938). Using the accommodation coefficient method as an index to the presence of the surface film, this author showed that nitrogen gas at 10^{-4} mms. of mercury pressure was rapidly adsorbed by tungsten at room temperature.

The Condensation of Nitrogen on Tungsten.

Previously recorded work by E. K. Rideal and the author (Bosworth and Rideal, 1937) showed that the adsorption of nitrogen is associated with a change of potential of the tungsten surface. The equilibrium film exhibits a contact potential of $-1\cdot38$ volts relative to a clean surface. Taking the work function of tungsten at 300° K. as $4\cdot56$ volts (Becker and Brattain, 1934 ; Reimann, 1934), this means that the work function of a WN surface is $5\cdot94$ volts.

Before further study of the properties of this film is undertaken, it is most desirable to know how the work function for an incomplete nitrogen film varies with the fraction of the surface covered (θ). To a filament previously cleaned by flashing a regulated stream of nitrogen gas at low pressure was admitted and the change of contact potential followed as the film built up. The pressure of nitrogen in the contact potential tube was measured by means of an ionisation gauge. Let p be this pressure, t the time elapsing since admission of nitrogen, and let υ be the contact potential relative to a clean surface, i.e. we take $\upsilon=0$ when $t=0$. The results of experiments on condensation are given in graphical form in Figure 1, where υ is plotted against $\int p\,dt$. The curve is presented in two portions. In portion A the abscissa, $\int p\,dt$, has a scale of $0\cdot1$. In portion B the scale of the abscissa is unity.

During the study recorded in Figure 1, the whole of the contact p.d. tube was immersed in liquid air. At a temperature of 90° K. it would seem reasonable to assume that the film formed was of an immobile nature. The theory of the kinetics of the formation of an immobile film from a bimolecular gas has been given by J. K. Roberts (1938).

On the premises of the kinetic theory of gases it can be shown that the number (n) of molecules striking unit area in unit time at an (absolute) temperature T and pressure p is given by :

$$n=\frac{p}{\sqrt{2\pi m\mathbf{k}T}},$$

where m is the mass of the molecule concerned and $\mathbf{k}$ is the Boltzmann gas constant. The expression above holds only under conditions of pressure so low

that true molecular flow is obtained. It does not apply at ordinary pressures. The pressures obtained during the experiments described in this paper are all well within the region of molecular flow. If a diatomic molecular compound is used the number of atoms striking unit area in unit time is :

$$\frac{2p}{\sqrt{2\pi m\mathbf{k}T}}.$$

Roberts assumed that when a diatomic molecule comes into collision with a solid surface it can condense only if it strikes two neighbouring bare spaces. We will denote by θ the fraction of the surface covered and by n_s the number of

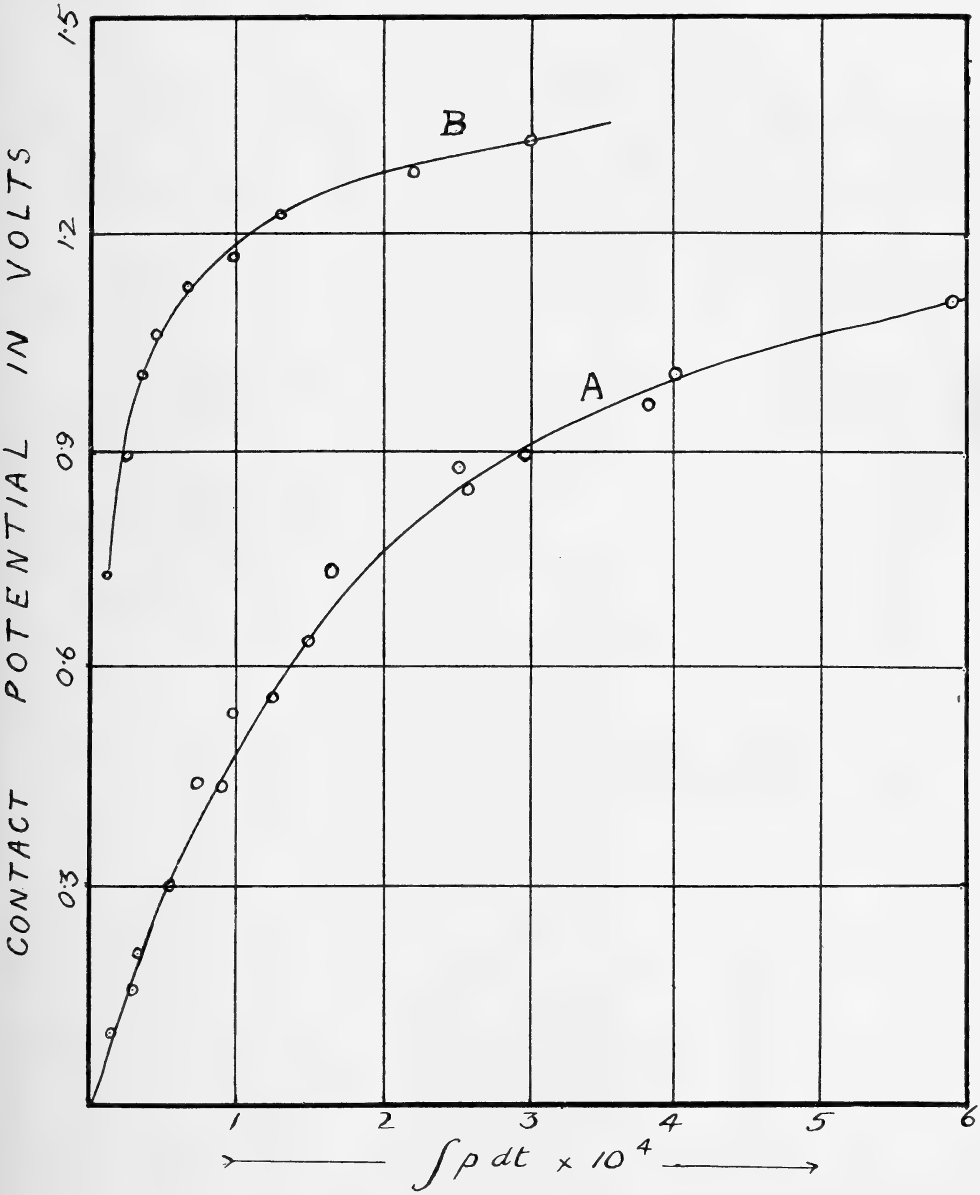

Fig. 1.

spaces per unit area available for adsorption. It follows that the rate at which the surface film is built up is given by:

$$\frac{d\theta}{dt}=\frac{2}{n_s}\,\frac{\alpha p}{\sqrt{2\pi m\mathbf{k}T}}\,\varphi(\theta)\ \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

where α, the so-called condensation coefficient, is the probability that a collision under favourable conditions will result in condensation. The value of α will involve such factors as the relative orientation of the incident molecule and the surface. In what follows we will assume therefore that α does not vary with θ. The function $\varphi(\theta)$ in equation (1) determines, at any surface concentration, the probability that two lattice points selected at random are bare. This particular function has been derived on theoretical grounds by Roberts (*loc. cit.*). The time t required at a pressure p to attain a given value of θ is given by integrating expression (1). Thus we find

$$\int_o^\theta \frac{d\theta}{\varphi(\theta)}=\frac{2}{n_s}\,\frac{\alpha p}{\sqrt{2\pi m\mathbf{k}T}}\,t.\ \ldots\ldots\ldots\ldots\ldots\ldots\ (1a)$$

In the event of the pressure p varying with the time, we may write:

$$\int_o^\theta \frac{d\theta}{\varphi(\theta)}=R(\theta)=\frac{2}{n_s}\,\frac{\alpha}{\sqrt{2\pi m\mathbf{k}T}}\int p\,dt.\ \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

This equation may be rewritten in the form:

$$\theta=\mathrm{I}\left(\left\{\frac{2}{n_s}\,\frac{\alpha}{\sqrt{2\pi m\mathbf{k}T}}\right\}\int p\,dt\right)=\mathrm{I}(k\int p\,dt),\ \ldots\ldots\ldots\ldots\ (3)$$

where I is the inverse function of R. The value of θ can thus be calculated from the measured values of $\int p\,dt$ provided the expression in braces, written as k, is known. In this expression there are two unknown factors, viz. α and n_s. For hydrogen and oxygen films on tungsten, n_s has been shown to be $1\cdot424\times10^{15}$, but there is no experimental evidence that this value also holds in the case of the nitrogen films. If, for example, in the surface compound formed the nitrogen atoms have their normal valence we might expect each nitrogen atom to replace three hydrogen atoms, in which case n_s would be $4\cdot81\times10^{14}$. On the other hand, however, oxygen atoms on the surface, notwithstanding the divalence of oxygen, occupy the same space as hydrogen atoms. We shall take as the value of n_s for nitrogen films the quantity.

$$\frac{1}{z}\ 1\cdot424\times10^{15},$$

where z represents the effective valence of the nitrogen adatoms or the number of elementary spaces on the surface occupied by one nitrogen atom.

The method of calculating θ from $\int p\,dt$ follows the procedure already described (Bosworth, 1945) apart from the use of the revised table of values for the function of $R(\theta)$ (Roberts, 1938). A value of k, in equation (3), is selected and from the curve shown in Figure 1 a θ versus υ curve is calculated. In general the resultant curve will show a pronounced inflection at about $\theta=\frac{1}{2}$. It is assumed that curves of this nature can have no physical significance and that the value of k which avoids this inflection (there is only one such value) is the correct one. For the data given in Figure 1 the required value of k becomes:

$$6\cdot0\times10^4 \text{ reciprocal (mms. of Hg}\times\text{secs.).}$$

We therefore have, from equation (3),

$$\frac{2z}{1\cdot424\times10^{15}}\ \frac{7\cdot075\times10^{22}\alpha}{\sqrt{28T}}.=6\cdot0\times10^4.$$

28 is the molecular weight of nitrogen and T the temperature of the gas incident on to the surface may be taken as 90° K. We therefore find that :

$$z\alpha = 3 \times 10^{-2}.$$

Thus if the nitrogen atoms occupy the same space on the surface as hydrogen atoms the condensation coefficient is about 1 in 30. If one nitrogen atom occupies the same space as three hydrogen atoms, the condensation coefficient is 1 in 100.

The υ versus θ curve obtained in the estimation of this value of the condensation coefficient is given in Figure 2. The curve is practically linear, or the work function varies almost linearly with the fraction of the surface covered. In other words the dipole moment of the adsorbed nitrogen is practically independent of the fraction of the surface covered, being in point of fact only 4% less for the complete film than for a very dilute film.

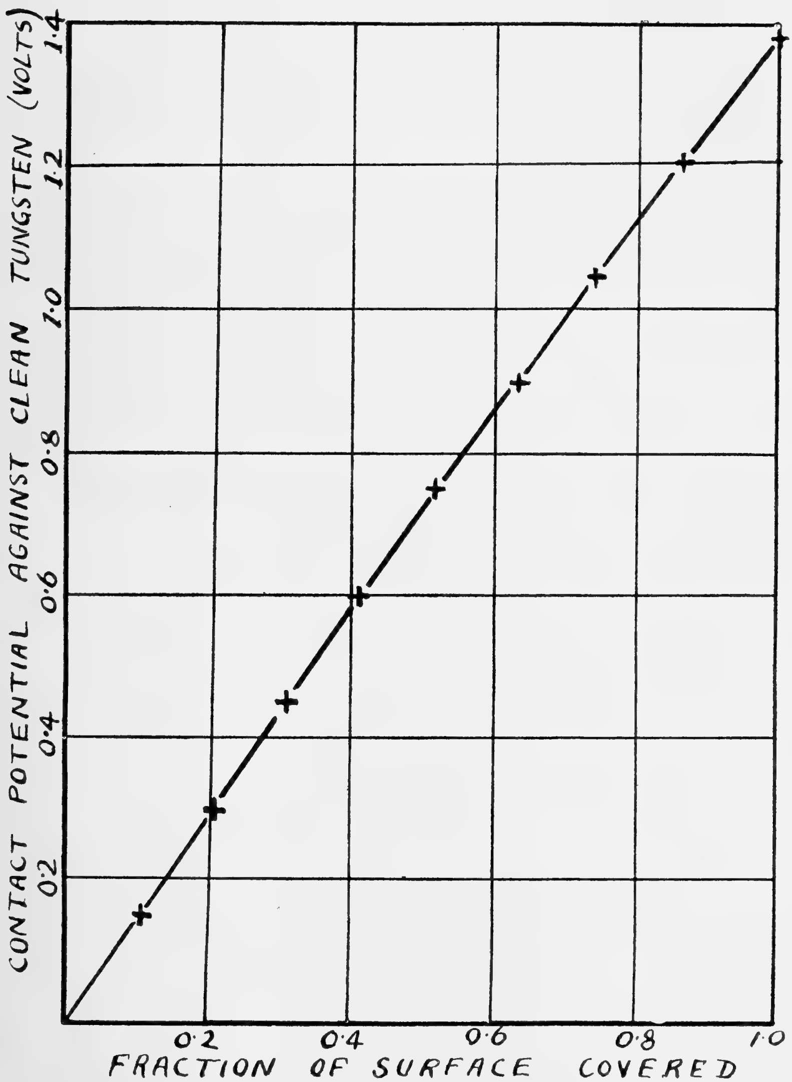

Fig. 2.

Evaporation of Nitrogen Films.

In the study of the evaporation of these films the surface under test was heated to a suitable temperature between 740° K. and 1180° K. and the change of the contact potential difference was recorded as a function of the time for a number of fixed temperatures. Curves showing this change have been recorded by Bosworth and Rideal (1937). By reading from these curves the times taken at different temperatures for a given change in the contact potential and using the vapour pressure equation it is possible to calculate the heat of evaporation E of the film at any stage of the evaporation process. In the paper referred to above E has been given as a function of the contact potential υ relative to the clean surface. By using the relationship between θ and υ shown in Figure 2

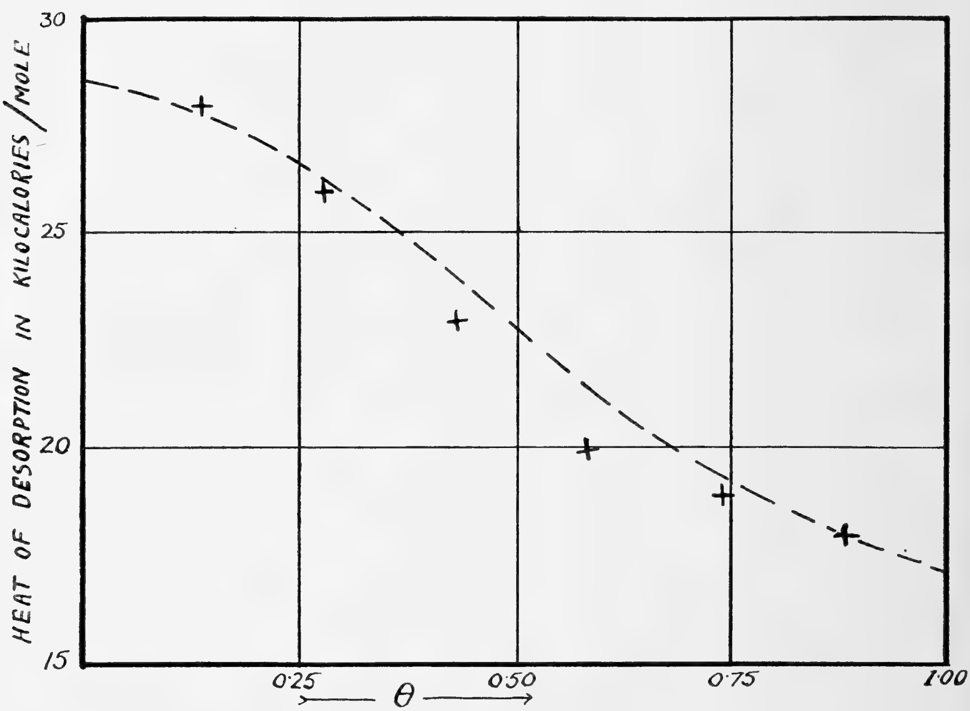

Fig. 3.

of the present paper, it is now possible to give the heat of evaporation E as a function of the fraction θ of the surface covered. The resultant relationship is shown by the point plotted in Figure 3. It will be noted that the heat of evaporation is comparatively small and that the points are approximately symmetrically disposed with respect to the ordinate $\theta=0\cdot5$. The interpolated value at $\theta=0$ is 29,000 calories per gram molecule, and at $\theta=1$, 17,000 calories per gram molecule.

A theory of the variation of the heat of adsorption with degree of surface packing has been given by Roberts (1938). The theoretical relationship between E and θ is quite different according as the film formed is mobile or immobile. Roberts was principally concerned with heats of adsorption at room temperature. In this paper we are concerned with heats of desorption at considerably higher temperatures, and since all earlier experiments have indicated that two-dimensional mobility is a property acquired at temperatures often considerably

below the vapourising point it seemed reasonable to assume that the theory appropriate to the mobile film should be the one to consider in the present instance.

For condensation on the 100 plane Roberts gives for the equation for adsorption with interaction in a mobile film:

$$\frac{\mathsf{E}-\mathsf{E}_0}{v}=-2\left[1-\frac{1-2\theta}{\{1-4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}}\right], \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

where E is the heat of adsorption at concentration θ,

E_0 the heat of adsorption at concentration 0,

v the energy of interaction between two neighbouring adatoms,

$$8v=\mathsf{E}_0-\mathsf{E}_1,$$

E_1 the heat of evaporation for a monolayer ($\theta=1$),

and η is $\exp(-v/kT)$.

For nitrogen on tungsten films

$$v=\frac{1}{8}(29{,}000-17{,}000),$$

$$=1{,}500 \text{ calories per gram molecule,}$$

or $$=1\cdot 0\times 10^{-13} \text{ ergs per pair of atoms,}$$

so that at the mean temperature of evaporation, viz. 950° K.,

$$\eta=\exp(-0\cdot 77)=0\cdot 46.$$

Using these figures for η and v, we may now plot E as a function of θ. The resultant relationship is shown in the broken curve in Figure 3. The deviation of the experimental points from this theoretical curve is probably not outside the experimental error. We may conclude therefore that the nitrogen film, while acting as immobile at 90° K., is effectively mobile at 740° K. (the lowest temperature at which evaporation was studied), and at all higher temperatures.

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THE CALCULATION OF THE GROUND MOVEMENT FOR THE INITIAL IMPULSES OF GALITZIN SEISMOGRAPHS.

By D. J. K. O'Connell, S.J., M.Sc., D.Ph.

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For a seismograph that is properly designed and is kept in good adjustment it is possible to obtain formulæ relating the amplitude of the earth motion to the recorded motion of the seismograph. If it can be assumed that the earth motion is simple harmonic (and this is often at least approximately the case), it is comparatively simple to deduce the earth motion when sufficient time has elapsed after the initial impulse for the contribution of the seismograph itself to die away. It is a much more difficult problem to determine the earth motion for the initial impulse of a new phase on the record. Various solutions have been attempted. For the Galitzin seismographs with galvanometric registration the best analysis of the problem so far available is that given by Galitzin himself (1914). Tables were computed by Galitzin to facilitate the application of his results. The object of this paper is to extend these tables.

In all that follows it is assumed that the constants of the seismograph have been properly determined, that the periods of the seismograph and galvanometer are identical, and that both are critically damped. In practice, small deviations from these conditions may be tolerated.

The earth motion is assumed to be of the form

$$x = x_m \sin pt, \qquad (1)$$

where x_m is the maximum amplitude,

$$p = \frac{2\pi}{T_e}, \qquad (2)$$

and T_e=period of earth motion.

The motion of the pendulum can be shown to take the form

$$\theta'' + 2n\theta' + n^2\theta + \frac{x''}{l} = 0 \qquad (3)$$

where the dashes denote differentiation with respect to time,

$$n = \frac{2\pi}{T} \qquad (4)$$

T=period of pendulum,

and l=reduced pendulum length, a constant for each seismograph.

The motion of the galvanometer is represented by

$$\varphi'' + 2n\varphi' + n^2\varphi = -k\theta', \qquad (5)$$

k being one of the seismograph constants.

Galitzin integrated these equations and finally, after a long analysis, obtained, equivalently, the following expression for y, the measured trace amplitude:

$$y = 4V_s x_m F(\xi), \qquad (6)$$

where V_s=synchronous magnification—a quantity defined by Sohon (1932), p. 94—and obtained when determining the constants of the seismograph,

$$\xi = pt \qquad (7)$$

$$F(\xi) = e^{-u\xi}(a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3) + g\cos\xi + h\sin\xi \qquad (8)$$

$$\left.\begin{array}{ll} a_0 = \dfrac{1-6u^2+u^4}{(1+u^2)^4} & a_3 = \dfrac{-u^3}{6(1+u^2)} \\ a_1 = \dfrac{-u(3-u^2)}{(1+u^2)^3} & g = -a_0 \\ a_2 = \dfrac{u^2(3+u^2)}{2(1+u^2)^2} & h = \dfrac{4u(1-u^2)}{(1+u^2)^4} \end{array}\right\} \qquad (9)$$

and

$$u = T_e/T \qquad (10)$$

The exponential term represents the part of the motion due to the initial disturbance of the seismograph. It will be seen that, when sufficient time has elapsed, this term becomes very small and may be neglected, so that the expression for $F(\xi)$ becomes much simpler. For the first maximum, however, this term must be included.

From equation (6) y is a maximum when $F(\xi)$ is a maximum. The problem then is to solve the equation

$$\frac{dF(\xi)}{d\xi} = 0 \qquad (11)$$

What is required is the smallest positive root of this equation, corresponding to the first maximum of the motion on the record. Call this root ξ_m.

Galitzin solved this equation for a series of values of u, and tabulated ξ_m and the corresponding values of $F(\xi_m)$, with u as argument. The amplitude of the earth motion can then be obtained from $F(\xi_m)$ by equation (7).

Galitzin's table goes from u=0 to u=1. As the period of Galitzin's seismographs was 24 seconds, the table covers earth motions up to 24 seconds, which is adequate. The tendency nowadays is to use Galitzin seismographs with shorter periods. The Galitzins at Riverview Observatory[1] are kept at periods of about 12 seconds, so that at Riverview Galitzin's table suffices for earth periods of up to 12 seconds. In practice one has to deal with longer earth periods. Accordingly more extended tables were computed by the writer for use at Riverview. The computations are long and tedious. As the results should prove useful to other users of Galitzin seismographs, it was thought well to publish them.

Equation (11) was solved for a number of values of u from u=1·0 to u=2·0. Values of ξ_m for intermediate values of u were obtained graphically and $F(\xi_m)$ was then obtained from equation (8).

The results are given in Table I, which is an extension of Galitzin's table.

TABLE I.

u	ξ_m	$F(\xi_m)$	u	ξ_m	$F(\xi_m)$
1·00	1·012	0·104	1·60	0·709	0·046
1·10	0·946	0·089	1·70	0·674	0·041
1·20	0·888	0·077	1·80	0·642	0·037
1·30	0·836	0·067	1·90	0·613	0·033
1·40	0·789	0·059	2·00	0·587	0·030
1·50	0·747	0·052			

[1] These seismographs were constructed in Sydney under the direction of Dr. E. F. Pigot, S.J., mainly at the Royal Australian Navy Wireless and Electrical Works, Randwick.

In practice the most useful table is that given by Sohon (1932, p. 110). It is adapted from Galitzin's table and gives $1/4uF(\xi_m)$ with u as argument. For the convenience of users this function is given in full in Table II, the values up to $u=1\cdot 0$ being taken from Sohon's table, the remainder being computed by the writer.

TABLE 2.

Factor for the Reduction of Impulses for Galitzin Seismographs.

u	$\frac{1}{4uF(\xi_m)}$	u	$\frac{1}{4uF(\xi_m)}$	u	$\frac{1}{4uF(\xi_m)}$	u	$\frac{1}{4uF(\xi_m)}$
0·01	13·30	0·51	1·73	1·01	2·42	1·51	3·24
0·02	6·36	0·52	1·74	1·02	2·43	1·52	3·26
0·03	4·99	0·53	1·75	1·03	2·45	1·53	3·28
0·04	3·96	0·54	1·76	1·04	2·46	1·54	3·30
0·05	3·34	0·55	1·77	1·05	2·47	1·55	3·32
0·06	2·94	0·56	1·78	1·06	2·49	1·56	3·34
0·07	2·65	0·57	1·79	1·07	2·51	1·57	3·35
0·08	2·44	0·58	1·80	1·08	2·52	1·58	3·37
0·09	2·28	0·59	1·82	1·09	2·54	1·59	3·38
0·10	2·15	0·60	1·83	1·10	2·55	1·60	3·40
0·11	2·05	0·61	1·84	1·11	2·57	1·61	3·41
0·12	1·97	0·62	1·85	1·12	2·59	1·62	3·43
0·13	1·91	0·63	1·86	1·13	2·60	1·63	3·45
0·14	1·85	0·64	1·88	1·14	2·62	1·64	3·46
0·15	1·81	0·65	1·89	1·15	2·64	1·65	3·48
0·16	1·77	0·66	1·90	1·16	2·65	1·66	3·50
0·17	1·74	0·67	1·91	1·17	2·67	1·67	3·52
0·18	1·71	0·68	1·92	1·18	2·69	1·68	3·53
0·19	1·68	0·69	1·94	1·19	2·70	1·69	3·55
0·20	1·66	0·70	1·95	1·20	2·72	1·70	3·57
0·21	1·64	0·71	1·97	1·21	2·73	1·71	3·59
0·22	1·62	0·72	1·98	1·22	2·75	1·72	3·61
0·23	1·61	0·73	2·00	1·23	2·76	1·73	3·62
0·24	1·60	0·74	2·01	1·24	2·78	1·74	3·64
0·25	1·59	0·75	2·02	1·25	2·79	1·75	3·66
0·26	1·59	0·76	2·04	1·26	2·81	1·76	3·68
0·27	1·58	0·77	2·06	1·27	2·83	1·77	3·69
0·28	1·58	0·78	2·07	1·28	2·85	1·78	3·71
0·29	1·59	0·79	2·08	1·29	2·86	1·79	3·73
0·30	1·59	0·80	2·10	1·30	2·88	1·80	3·74
0·31	1·59	0·81	2·11	1·31	2·90	1·81	3·76
0·32	1·59	0·82	2·12	1·32	2·91	1·82	3·78
0·33	1·60	0·83	2·13	1·33	2·93	1·83	3·80
0·34	1·60	0·84	2·15	1·34	2·95	1·84	3·82
0·35	1·60	0·85	2·17	1·35	2·96	1·85	3·84
0·36	1·61	0·86	2·18	1·36	2·98	1·86	3·86
0·37	1·61	0·87	2·21	1·37	3·00	1·87	3·88
0·38	1·62	0·88	2·22	1·38	3·01	1·88	3·90
0·39	1·62	0·89	2·23	1·39	3·03	1·89	3·92
0·40	1·63	0·90	2·24	1·40	3·05	1·90	3·94
0·41	1·63	0·91	2·25	1·41	3·07	1·91	3·95
0·42	1·64	0·92	2·26	1·42	3·08	1·92	3·97
0·43	1·65	0·93	2·28	1·43	3·10	1·93	3·99
0·44	1·66	0·94	2·29	1·44	3·12	1·94	4·01
0·45	1·66	0·95	2·31	1·45	3·13	1·95	4·03
0·46	1·67	0·96	2·32	1·46	3·15	1·96	4·05
0·47	1·68	0·97	2·34	1·47	3·17	1·97	4·06
0·48	1·69	0·98	2·36	1·48	3·19	1·98	4·07
0·49	1·70	0·99	2·38	1·49	3·21	1·99	4·09
0·50	1·71	1·00	2·40	1·50	3·22	2·00	4·10

To obtain the actual magnification for an impulse, divide the synchronous magnification (V_s) by the above factor.

Summary.

Galitzin derived a method of computing the ground movement for initial impulses on his seismographs. The tables he gives were designed for seismograph periods of 24 seconds. For Galitzin seismographs with shorter periods, as generally used nowadays, Galitzin's tables are inadequate. Extended tables have been computed and are given here.

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THE EIGEN-VALUE PROBLEM OF HILL'S EQUATION.[1]

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(Communicated by Professor V. A. Bailey.)

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1. Introduction.

In classical mechanics the motion of a particle P is described by its co-ordinates x, y, z, which are functions of the time parameter t. According to the laws of dynamics these functions are found as the solution of a system of differential equations of the second order for a given set of initial conditions. In quantum mechanics this " time-table principle " is replaced by a statistical principle. Here it is impossible to determine the accurate position of P at any instant t; rather the probability for the particle P of mass m to be at the time t in a certain neighbourhood N of a point (x, y, z) is determined as a certain function of N. It is expressed by the integral

$$\iiint_{\mathrm{N}} \psi\bar{\psi}\, dx\, dy\, dz = [\psi\bar{\psi}]_{\mathrm{Q}}\, |\mathrm{N}|$$

where $\psi=\psi(x, y, z, t)$ is a certain complex function, the so-called " probability function ", $\bar{\psi}$ its conjugate complex value, $|\mathrm{N}|$ the volume of N, and $[\psi\bar{\psi}]_{\mathrm{Q}}$ the value of the non-negative function $\psi\bar{\psi}=|\psi|^2$ at a certain mean point Q of N. The function ψ has to satisfy Schroedinger's differential equation

$$\Delta\psi - \frac{2m}{h^2}\, v . \psi = \frac{2m}{ih}\, \frac{\partial\psi}{\partial t} \tag{1, 1}$$

where $v=v(x, y, z)$ is the potential of the field of the force in which P moves, Δ the Laplace operator in rectangular cartesian co-ordinates x, y, z, and $2\pi h$, in the notation of Weyl (1931a) the Planck quantum constant. Since the particle has always to be somewhere in the space, the function ψ, according to its physical interpretation, has to satisfy the condition

$$\iiint \psi\bar{\psi}\, dx\, dy\, dz = 1 \tag{1, 2}$$

where the integral is to be taken over the whole of space.

Physically the probability function is uniquely defined apart from a factor of modulus one. To determine it mathematically, the two conditions (1, 1) and (1, 2) are of course not sufficient; the function ψ has, however, to satisfy certain initial and boundary conditions by which a special problem is made definite.

2. The Eigen-Value Problem.

To solve Schroedinger's equation (1, 1) one may use the classical idea of Bernoulli's solution of the equation of the vibrating string, and construct the desired solution by superposition of " standing waves ", i.e. special solutions of the form

$$\psi = \varphi(x, y, z) \,.\, \chi(t).$$

[1] Read at two consecutive meetings of the Adelaide University Mathematical Society June 28 and July 5, 1945.

It follows from (1, 1) that

$$\frac{\chi'(t)}{\chi(t)} = -\frac{i}{h}\lambda \tag{2, 1}$$

is independent of the variables x, y, z, t and therefore

$$\chi(t) = ce^{-\frac{i}{h}\lambda t}$$

where c is constant. The real constant λ is the energy constant, usually denoted by E. For the function $\varphi = \varphi(x, y, z)$, i.e. the amplitude of the standing wave, which is independent of the time t, one has at once the differential equation

$$\frac{h^2}{2m}\Delta\varphi - v \cdot \varphi = -\lambda\varphi.$$

If herein one replaces x, y, z by $\frac{h}{\sqrt{2m}}x, \ldots$ respectively one obtains

$$\Delta\varphi + (\lambda - v)\varphi = 0. \tag{2, 2}$$

Problems in various parts of mathematical physics require the solution of (2, 2) for certain boundary conditions. In classical theories (vibration problems, potential theory) "boundary values" of the solution φ of a partial differential equation are prescribed on a certain closed surface surrounding or limiting the domain where the function φ is to be considered. Then, in general, an infinite set of discrete values of λ exists for which there is a solution φ that satisfies the boundary conditions. These values are the "eigen-values," the corresponding solutions are the "eigen-functions" of the problem. The set of all eigen-values is called the "spectrum".

Mutatis mutandis these statements and definitions remain valid if one or both of the variables y, z do not occur in the formulation of the problem. In particular in the one-dimensional case where $\varphi = \varphi(x)$ depends on the variable x only, the boundary conditions prescribe values of φ at the two endpoints a, b of an interval $\langle a, b \rangle$ (i.e. $a \leqslant x \leqslant b$) on the x-axis.

It is typical of the problems of quantum physics that the solution of (2, 2) is to be found in unlimited space. Boundary conditions here consist in a more or less definite prescription concerning the "values of φ at infinity". There are several possibilities; for instance:

(i) Limits of $\varphi(x, y, z)$ are prescribed if the point (x, y, z) approaches infinity in a certain well-defined way.

(ii) If the existence of limits of φ is not postulated, it may be required that φ is bounded throughout the whole of space.

Values of λ for which (2, 2) has a solution that satisfies such a degenerate boundary condition are again called eigen-values. By analogy with the case of a limited field where boundary values are prescribed on the surrounding surface we may expect a discrete spectrum in the case (i). This is verified, for instance, in the well-known (one-dimensional) case of the linear oscillator; one has to solve the ordinary differential equation

$$\frac{d^2\varphi}{dx^2} + (\lambda - x^2)\varphi = 0$$

for the degenerate boundary conditions

$$\varphi(-\infty) = 0, \quad \varphi(\infty) = 0.$$

The eigen-values of this problem are

$$\lambda = 2n + 1 \qquad (n = 0, 1, 2, \ldots)$$

and the corresponding eigen-functions

$$\varphi_n(x) = e^{-\frac{1}{2}x^2} H_n(x)$$

where

$$H_n(x) = (-1)^n e^{x^2} \cdot \frac{d^n e^{-x^2}}{dx^n}$$

is the n-th Hermitean polynomial.

In the case (ii), however, an elementary example shows that the spectrum will no longer be discrete. Again it will be sufficient to consider a one-dimensional example. If in (2, 2) $v \equiv 0$, one has the equation

$$\frac{d^2\varphi_0}{dx^2} + \lambda\varphi_0 = 0. \tag{2, 3}$$

Every solution $\varphi_0 = \varphi_0(x)$ of this equation is a linear combination of cos $(\sqrt{\lambda}x)$ and sin $(\sqrt{\lambda}x)$ with constant coefficients. Therefore $\varphi_0(x)$ is bounded if and only if $\lambda > 0$. The spectrum is formed here by the continuous set of all positive real numbers λ.

In general, in the case (ii), the spectrum of the eigen-values turns out to be "sectionally continuous". This means that there is a finite or infinite number of intervals on the λ-axis all points of which are eigen-values. The mathematical study of this physically important phenomenon (cf. Courant-Hilbert, 1931*b*). is the object of the present paper. In the discussion of the details we shall restrict ourselves to the one-dimensional case where $v = v(x)$ depends on the variable x only and moreover is bounded and periodic. This case is of independent importance in physics (cf. Frank-Mises, 1935*b*; Strutt, 1932*b*). It has been treated from several different points of view, and also in connection with more general questions (cf. Strutt, 1932*a*). The most straightforward method has been developed in a recent interesting paper by H. A. Kramers (1935); we take this as a guide for the present exposition, at the same time completing some of its mathematical details in a way which lends itself to generalizations to be dealt with in a later paper.

3. Hill's Equation and Floquet's Theory.

By the last mentioned restrictions we are led to consider the following ordinary linear homogeneous differential equation of the second order·

$$\frac{d^2\varphi}{dx^2} + (\lambda - v(x))\varphi = 0 \tag{3, 1}$$

where $v = v(x)$ is a function, bounded and continuous for all real x, and periodic with the period p:

$$v(x+p) = v(x).$$

The boundary conditions to be assumed here require the solution $\varphi = \varphi(x)$ of (3, 1) to be bounded for all real x. *Accordingly* λ *is an eigen-value of the problem if a bounded solution*

$$\varphi(x) = \varphi(x\,;\lambda)$$

of (3, 1) *can be found for this value* λ. While v and λ are supposed to be real, complex solutions $\varphi(x)$ are admitted.[2]

We begin with a few general remarks on the differential equation

$$\varphi'' + g(x)\varphi = 0 \tag{3, 2}$$

[2] The equation (3, 1) is called Hill's differential equation. It may be pointed out, however, that Hill's work was not concerned with the boundary value problem to be dealt with here, nor with any other boundary problem. Cf. Whittaker-Watson (1927*a*).

where $g(x)$ is a bounded real periodical function with the period p, later on to be identified with $\lambda - v(x)$. Let $\varphi_1(x)$, $\varphi_2(x)$ be a basis of (3, 2), i.e. a system of two linearly independent solutions so that with suitable (real or complex) constants c_1, c_2 any solution of (3, 2) appears in the form $c_1\varphi_1(x)+c_2\varphi_2(x)$. We denote the column of the basis functions by

$$\varphi(x) = \begin{bmatrix} \varphi_1(x) \\ \varphi_2(x) \end{bmatrix},$$

which then in the sense of the calculus with column matrices represents a solution of (3, 2). Because of the periodicity of $g(x)$ it is evident that also the column $\varphi(x+p)$ is a solution of (3, 2); therefore

(3, 3) $$\begin{cases} \varphi_1(x+p) = a_1^{\ 1}\varphi_1(x) + a_1^{\ 2}\varphi_2(x) \\ \varphi_2(x+p) = a_2^{\ 1}\varphi_1(x) + a_2^{\ 2}\varphi_2(x) \end{cases}$$

or briefly

(3, 3)′ $$\varphi(x+p) = A\varphi(x)$$

where

$$A = \begin{bmatrix} a_1^{\ 1} & a_1^{\ 2} \\ a_2^{\ 1} & a_2^{\ 2} \end{bmatrix}$$

is a regular matrix (i.e. the determinant $|A| \neq 0$) with constant elements $a_i^{\ j}$. It may be called the " period matrix " of the basis $\varphi(x)$. The period matrix is real if the basis $\varphi(x)$ is real. We shall start with a real basis.

Since in (3, 2) the coefficient of the first derivative is zero, it follows that the Wronskian determinant of a basis $\varphi(x)$, i.e. the determinant of the matrix

$$\Phi(x) = (\varphi(x) \ \ \varphi'(x)) = \begin{bmatrix} \varphi_1(x) & \varphi_1'(x) \\ \varphi_2(x) & \varphi_2'(x) \end{bmatrix}$$

is constant:

$$|\Phi(x)| = |\Phi(0)| \text{ for all } x.$$

Therefore, since by (3, 3)′,

(3, 4) $$\Phi(x+p) = A\Phi(x),$$

one has

(3, 5) $$|A| = 1.$$

Any basis $\varphi^*(x)$ of (3, 2) is obtained from a given basis $\varphi(x)$ by a linear homogeneous transformation with a (real or complex) constant regular matrix T:

$$\varphi^*(x) = T\varphi(x).$$

In order to find the period matrix A^* of the basis $\varphi^*(x)$ we form

$$\varphi^*(x+p) = T\varphi(x+p) = TA\varphi(x) = TAT^{-1}\varphi^*(x).$$

Thus we have

(3, 6) $$A^* = TAT^{-1}.$$

This means that *every change of the basis entails a similarity transformation of the corresponding period matrix.*

Now we have to investigate under what conditions the solutions of (3, 2) are bounded. From (3, 3)′ one has for any integer k the relation

(3, 7) $$\varphi(x+kp) = A^k\varphi(x).$$

Hence the basis $\varphi(x)$, and therefore any solution of (3, 2), is certainly bounded if and only if the sequence of the matrices A^k ($k=0, \pm 1, \pm 2, \ldots$) is bounded (i.e. the elements of the matrix powers A^k are members of bounded sequences). It may happen, however, that there is a bounded solution $\tilde{\varphi}_1(x)$ and an unbounded

one, $\tilde{\varphi}_2(x)$. For the decision we shall choose a basis $\tilde{\varphi}(x)$ such that the corresponding period matrix $\tilde{A}$ appears in its *similarity normal form*, the so-called *canonical form.* All possible canonical forms of the period matrix A can be derived from the following theorem of linear algebra which is proved in the appendix :

Theorem I. *For every real two-rowed square matrix A a real or complex regular matrix T can be found such that*

$$TAT^{-1}=\tilde{A}=\begin{pmatrix}\alpha_1 & 0\\ \alpha_0 & \alpha_2\end{pmatrix}$$

where α_1, α_2 are the characteristic roots of A, i.e. the roots of the characteristic polynomial

$$|\xi E-A|=\xi^2-f\xi+|A| \qquad \text{where } E=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

(*a*) *If $\alpha_1\neq\alpha_2$, or $\alpha_1=\alpha_2$ and A symmetric (i.e. $a_1{}^2=a_2{}^1$, whence follows that $a_1{}^2=0$ and thus $A=\alpha_1E$) one can reach by suitable choice of T, or one has automatically, $\alpha_0=0$.*

(*b*) *If $\alpha_1=\alpha_2$ and $A\neq\alpha_1E$, one has $\alpha_0\neq0$ for every choice of T, and one can reach $\alpha_0=1$, always ; by means of a real T if $\alpha_0>0$.*

Note.—The number α_0, if it is reduced to 0 or 1, may be called the " character " of A ; it is a non-rational similarity invariant of A. The rational similarity invariants of a matrix A are the coefficients of its characteristic polynomial, viz. the trace and the determinant of A :

$$f=\mathrm{tr}A=a_1{}^1+a_2{}^2=\alpha_1+\alpha_2$$
$$|A|=a_1{}^1a_2{}^2-a_1{}^2a_2{}^1=\alpha_1\alpha_2.$$

In the present case we have $|A|=1$; hence, if $\alpha_1=\alpha_2$ it follows that $\alpha_1=\varepsilon=\pm1$. Therefore the following normal forms of A come into question

(*a*) $$\tilde{A}=\begin{pmatrix}\alpha_1 & 0\\ 0 & \alpha_1^{-1}\end{pmatrix} \qquad \text{if } \alpha_0=0,$$

(*b*) $$\tilde{A}=\begin{pmatrix}\varepsilon & 0\\ 1 & \varepsilon\end{pmatrix} \qquad \text{if } \alpha_0=1.$$

The discriminant of the characteristic polynomial is here f^2-4. Thus we can state

(1) If $f=\pm2$ one has $\alpha_1=\varepsilon$ and normal form (*a*) or (*b*).

(2) If $|f|<2$ one has $|\alpha_1|=1$ and normal form (*a*).

(3) If $|f|>2$ one has α_1 real and $\neq\varepsilon$, and normal form (*a*).

In the case (*a*) the sequence A^k is bounded, and thus the corresponding basis $\varphi(x)$ and any solution of (3, 2) bounded, *if and only if* $|\alpha_1|=1$; moreover $\varphi(x)$ is periodical with the period kp if and only if α_1 is a k-th root of unity (cf. section 6).

In the case (*b*) one has

$$\tilde{A}^k=\begin{pmatrix}\varepsilon^k & 0\\ k\varepsilon^{k-1} & \varepsilon^k\end{pmatrix}$$

and therefore the sequence of the powers of $A=T^{-1}\tilde{A}T$ certainly not bounded. But the basis $\tilde{\varphi}(x)$ to which $\tilde{A}$ belongs consists here of a bounded periodical $\tilde{\varphi}_1(x)$ and an unbounded function $\tilde{\varphi}_2(x)$.

While the matrix A depends on the choice of the basis, the similarity invariants of the period matrix are the same, whatever the basis ; they therefore

depend on the coefficient functions $g(x)$ in (3, 2) only. If we turn to the equation (3, 1) this means that after the function $v(x)$ has been chosen in a definite way, the similarity invariants of A depend on the value of λ, the "eigen-value parameter", only. We call λ an r-fold eigen-value if r (and not more than r) linearly independent bounded solutions belong to λ. In this terminology the result of our consideration is

Theorem II.

(1) *If* $|f|=2$ $(\alpha=\varepsilon)$ *and* (*a*) $\alpha_0=0$ *then* $r=2$,
(*b*) $\alpha_0=1$ *then* $r=1$.

(2) *If* $|f|<2$ $(|\alpha_1|=1)$ *then* $r=2$.

(3) *If* $|f|>2$ (α_1 real $\neq\varepsilon$) *then* $r=0$, *i.e.* λ *is no eigen-value.*

4. Some Auxiliary Formulas.

The last theorem shows that for an accurate localization of the eigen-values we have to study the trace f of the period matrix A as a function of the eigen-value parameter λ; we write

$$f=f(\lambda)=a_1^1+a_2^2.$$

We saw that this function does not depend on the choice of a basis $\varphi(x)$ of the equation (3, 1). We shall have to consider also the elements a_i^j of A in dependence on λ; they are definite functions of λ, however, only after a definite basis

$$\varphi(x)=\varphi(x\,;\lambda)$$

has been chosen for each value of λ.

A basis $\varphi(x)$ is completely defined by the matrix

$$\Phi(0)=(\varphi(0)\ \ \varphi'(0))=C$$

of the "initial values" of $\varphi(x)$ and its first derivative $\varphi'(x)$ for $x=0$. If the initial matrix C is real, which we assume here, the corresponding basis $\varphi(x)$ is real; the determinant $|C|=c$ is the Wronskian of the basis. The period matrix A is found from (3, 4):

$$A=\Phi(x+p)\Phi(x)^{-1}\,;$$

because it is independent of x, we may substitute here for x the value 0 and obtain

$$A=\Phi(p)C^{-1}. \tag{4, 1}$$

Therefore, if $C=E$, we have

$$f=\varphi_1(p)+\varphi_2'(p). \tag{4, 2}$$

In order to discuss the behaviour of $f=f(\lambda)$ we need its first two derivatives $\dot{f}(\lambda)$ and $\ddot{f}(\lambda)$. Generally denoting by $\cdot$ the differentiation with respect to λ, we find from (3, 1)

$$\dot{\varphi}_j''(x)+(\lambda-v)\dot{\varphi}_j(x)=-\varphi_j(x) \qquad (j=1, 2), \tag{4, 3}$$

i.e. a non-homogeneous linear differential equation for the function.

$$\dot{\varphi}_j(x)=\frac{\partial\varphi_j(x)}{\partial\lambda}.$$

If now we assume the same initial matrix C for all values of λ, we have

$$\dot{\varphi}_j(0)=0, \qquad \dot{\varphi}_j'(0)=0.$$

The solution of (4, 3) for these initial values is, according to a well-known formula[3]

(4, 3)′
$$\dot\varphi_j(x)=\frac{1}{c}\int_o^x \begin{vmatrix} \varphi_1(x) & \varphi_1(t) \\ \varphi_2(x) & \varphi_2(t) \end{vmatrix} \varphi_j(t)dt$$

By differentiation with respect to x one has

(4, 3)″
$$\dot\varphi_j'(x)=\frac{1}{c}\int_o^x \begin{vmatrix} \varphi_1'(x) & \varphi_1(t) \\ \varphi_2'(x) & \varphi_2(t) \end{vmatrix} \varphi_j(t)dt.$$

Now we introduce the inner products of the basis functions $\varphi_j(x)$, i.e. the integrals

$$\omega_{ij}=\frac{1}{c}\int_o^p \varphi_i(t)\varphi_j(t)dt \qquad (i,\ j=1,\ 2).$$

Then $\omega_{21}=\omega_{12}$. Since $\varphi_1(x)$, $\varphi_2(x)$ are linearly independent, their Gram determinant is

(4, 4)
$$\delta=\omega_{11}\omega_{22}-(\omega_{12})^2>0.$$

From (4, 3)′ and (4, 3)″ it follows

$$\dot\varphi_j(p)=\omega_{2j}\varphi_1(p)-\omega_{1j}\varphi_2(p)$$
$$\dot\varphi_j'(p)=\omega_{2j}\varphi_1'(p)-\omega_{1j}\varphi_2'(p)$$

or in the matrix notation

$$\dot\Phi(p)=\Omega\,.\,\Phi(p) \qquad \text{where } \Omega=\begin{bmatrix} \omega_{12} & -\omega_{11} \\ \omega_{22} & -\omega_{12} \end{bmatrix}$$

Hence, still under the supposition that the initial matrix C does not depend on λ, one has by (4, 1)

(4, 5)
$$\dot A=\Omega\Phi(p)C^{-1}=\Omega A.$$

Because of (3, 5)

$$|\dot A|=\delta=|\Omega|.$$

Since

$$\Omega^2=-\delta E,$$

differentiation of (4, 5) leads to the relation

(4, 6)
$$\ddot A=\dot\Omega A+\Omega\dot A=(\dot\Omega+\Omega^2)A=(\dot\Omega-\delta E)A.$$

Thus we find the traces of $\dot A$ and $\ddot A$ to be

(4, 7)
$$\dot f(\lambda)=-\omega_{11}a_2^1+\omega_{12}(a_1^1-a_2^2)+\omega_{22}a_1^2$$

(4, 8)
$$\ddot f(\lambda)=-\dot\omega_{11}a_2^1+\dot\omega_{12}(a_1^1-a_2^2)+\dot\omega_{22}a_1^2-\delta\,.\,f(\lambda).$$

Finally we establish an inequality which will be used later on. According to the definition of ω_{12} one has

$$\dot\omega_{12}=\frac{1}{c}\int_o^p(\dot\varphi_1(x)\varphi_2(x)+\varphi_1(x)\dot\varphi_2(x))dx$$
$$=\frac{1}{c^2}\int_o^p\int_{t=0}^x(\varphi_1(x)\varphi_2(t)-\varphi_2(x)\varphi_1(t))(\varphi_1(x)\varphi_2(t)+\varphi_2(x)\varphi_1(t))dtdx$$
$$=\frac{1}{c^2}\int_o^p\int_o^x(\varphi_1(x)^2\varphi_2(t)^2-\varphi_2(x)^2\varphi_1(t)^2)dtdx.$$

---

[3] It is readily verified by differentiation.

Therefore

$$|\dot{\omega}_{12}| < \frac{1}{c^2} \int_o^p \int_o^x \varphi_1(x)^2 \varphi_2(t)^2 dt dx$$

$$< \frac{1}{c^2} \int_o^p \int_o^p \varphi_1(x)^2 \varphi_2(t)^2 dt dx = \omega_{11}\omega_{22}$$

or

(4, 9) $$-\omega_{11}\omega_{22} < \dot{\omega}_{12} < \omega_{11}\omega_{22}.$$

5. The Eigen-Value Intervals.

In order to obtain an approximate representation of the function $f(\lambda)$ we shall consider it first for large values of $|\lambda|$. In this case we may expect that the relatively small function v will not greatly affect the behaviour of the solutions $\varphi_j(x)$ of (3, 1). Thus, instead of (3, 1), we now solve for the same initial conditions the equation (2, 3), i.e.

(5, 1) $$\varphi_0'' + \lambda\varphi_0 = 0.$$

It can be shown (cf. Appendix) that if $\varphi(x)$ and $\varphi_0(x)$ are solutions of (3, 1) and (5, 1) respectively, for the same initial conditions, then within a certain interval of x-values the difference $|\varphi(x) - \varphi_0(x)|$ tends to zero if $\lambda \to \infty$. We express this by saying that within this interval $\varphi_0(x)$ gives an asymptotical representation of $\varphi(x)$.

The basis of (5, 1) for $C = E$ is

$$\varphi_{01}(x) = \cos(\sqrt{\lambda}x), \qquad \varphi_{02}(x) = \frac{1}{\sqrt{\lambda}} \sin(\sqrt{\lambda}x).$$

Hence the trace of the period matrix in real terms is by (4, 2)

(5, 2) $$f_0(\lambda) = \varphi_{01}(p) + \varphi'_{02}(p) = \begin{cases} 2\cos(\sqrt{\lambda}p) & \text{if } \lambda > 0\,; \\ 2\cosh(\sqrt{-\lambda}p) & \text{if } \lambda < 0. \end{cases}$$[4]

Thus we see that $f(\lambda)$ is very large positive for large negative values of λ, and that its graph in a rectangular λ, f-co-ordinate system approaches asymptotically the curve of the function $2\cos(\sqrt{\lambda}p)$ if λ becomes positive and increases indefinitely. This rough estimation leads to the conjecture that the function $f(\lambda)$ is generally described by the graph in Fig. 1. By making use of Kramers' arguments we shall now establish its essential features.

Firstly we state that there is certainly a least value such that for all values λ of a finite or infinite interval, $<\lambda_1, \lambda_2>$ (i.e. $\lambda_1 \leqslant \lambda \leqslant \lambda_2$ where $\lambda_1 < \lambda_2$) or $\lambda > \lambda_1$, one has $|f(\lambda)| \leqslant 2$. By theorem II these λ are eigen values of multiplicity $r \geqslant 1$. From the asymptotical representation of $f(\lambda)$ we expect that for $\lambda > \lambda_1$ this function has an infinity of relative minima and maxima. We shall show that

(1) The minimum values are all < -2;

(2) The maximum values are all $> +2$;

(3) There are no other stationary values of $f(\lambda)$.

Let $f(\lambda^*)$ be a stationary (extremum) value of $f(\lambda)$ such that the derivative $\dot{f}(\lambda^*) = 0$. We assume that the initial matrix C for the basis $\varphi(x) = \varphi(x\,; \lambda^*)$ is chosen so that the two functions $\varphi_1(x)$, $\varphi_2(x)$ are orthogonal over the period interval. Thus, for $\lambda = \lambda^*$, one has

$$\omega_{12} = 0.$$

[4] In the equation (5, 1) one has $v \equiv 0$ and therefore any real number is here a period of v. Since (5, 1) is taken as a substitute for (3, 1) where $v(x)$ is a function with the period p, it is natural to use this period also in the asymptotical representation of the trace $f_0(\lambda)$.

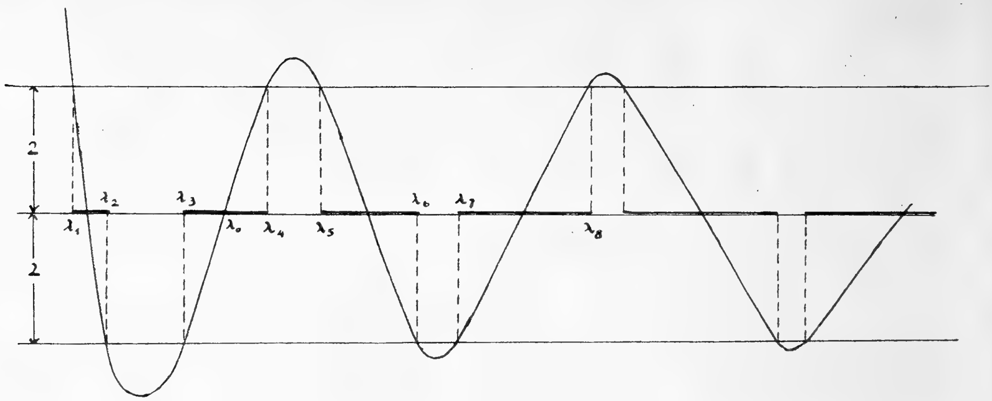

Fig. 1. (*After* Kramers, 1935.)

By (4, 7) the extremum condition then is

(5, 3) $$-\omega_{11}a_2^1+\omega_{22}a_1^2=0.$$

Since ω_{11}, ω_{22} are positive, it follows that a_2^1 and a_1^2 have equal signs :

$$a_1^2a_2^1 \geqslant 0.$$

With respect to (3, 5) this means that

$$a_1^1a_2^2 \geqslant 1.$$

Therefore also a_1^1 amd a_2^2 have equal signs.

If they are both positive one has

(5, 4) $$0 \leqslant (\sqrt{a_1^1}-\sqrt{a_2^2})^2 = a_1^1+a_2^2-2\sqrt{a_1^1}\sqrt{a_2^2} \leqslant a_1^1+a_2^2-2$$

and therefore

$$f(\lambda^*)=a_1^1+a_2^2 \geqslant 2.$$

Similarly, if a_1^1, a_2^2 are both negative, one has $f(\lambda^*) \leqslant -2$.

It remains to be shown that the stationary points λ^* actually give

a minimum if $f(\lambda^*)<0$, i.e. $\leqslant -2$;

a maximum if $f(\lambda^*)>0$, i.e. $\geqslant +2$.

First let us assume that $f(\lambda^*)>2$. Then the basis[5] $\varphi(x)$ can be chosen such that $a_1^2=a_2^1=0$ (cf. section 3), and by (4, 7) the necessary extremum condition is

$$\omega_{12}(a_1^1-a_2^2)=0.$$

Since $a_1^1=a_2^2$ would mean that $\alpha_1=\alpha_2=1$, or $f(\lambda^*)=2$, it follows again $\omega_{12}=0$. Hence we have by (4, 8)

$$\ddot{f}(\lambda^*)=\dot{\omega}_{12}(a_1^1-a_2^2)-\omega_{11}\omega_{22}(a_1^1+a_2^2).$$

As here a_1^1, a_2^2 are both positive, the second part of the inequality (4, 9) shows that if $a_1^1-a_2^2>0$, one has

$$\ddot{f}(\lambda^*)<\omega_{11}\omega_{22}(a_1^1-a_2^2-a_1^1-a_2^2)=-2\omega_{11}\omega_{22}a_2^2<0.$$

If $a_1^1-a_2^2<0$ the first part of (4, 9) shows that

$$\ddot{f}(\lambda^*)<-2\omega_{11}\omega_{22}a_1^1<0.$$

[5] The basis can certainly be chosen real since the characteristic roots of A are real (cf. theorem II).

Therefore $f(\lambda^*)$ is a relative maximum. Similarly, if $f(\lambda^*) < -2$ one has by (4, 9)

$$\ddot{f}(\lambda^*) > -2\omega_{11}\omega_{22}a_1^{\ 1} > 0 \ \ (\text{or } \ddot{f}(\lambda^*) > -2\omega_{11}\omega_{22}a_2^{\ 2} > 0)$$

which means that λ^* then is a minimum point.

It remains to consider the cases

$$f(\lambda) = a_1^{\ 1} + a_2^{\ 2} = \pm 2.$$

If $\lambda = \lambda^*$ is an extremum point for $f(\lambda)$, it follows from (5, 4) for an orthogonalized basis that

$$a_1^{\ 1} = a_2^{\ 2} = \pm 1,$$

and by (3, 5) $a_1^{\ 2}a_2^{\ 1} = 0$ whence because of (5, 3)

$$a_1^{\ 2} = a_2^{\ 1} = 0.$$

Therefore (4, 8) yields here

$$\ddot{f}(\lambda^*) = \mp 2\delta = \mp 2\omega_{11}\omega_{22}$$

saying that $f(\lambda^*)$ is a maximum or minimum.

If, however,

$$f(\lambda) = \pm 2, \ \lambda \neq \lambda^*, \tag{5, 5}$$

i.e. λ not a stationary point λ^*, we have

$$-\omega_{11}a_2^{\ 1} + \omega_{22}a_1^{\ 2} \neq 0.$$

Thus if we choose the basis such that $a_1^{\ 2} = 0$ (theorem I), then it will be impossible for $a_2^{\ 1}$ to be zero ; we are here in the case (1) (*b*) of theorem II, which means that the points $\lambda = \lambda_1, \lambda_2, \lambda_3, \lambda_4, \ldots$ which satisfy (5, 5), represent simple eigen-values.

Thus all facts represented by the above figure are established ; they may be expressed in form of the

Theorem III. *There is, in general, an infinite number of closed intervals on the λ-axis, viz.*

$$<\lambda_1, \lambda_2>, \ <\lambda_3, \lambda_4>, \ldots \ (\lambda_1 < \lambda_2 < \lambda_3 < \lambda_4 < \ldots)$$

consisting of eigen-values of the equation (3, 1) *to which a bounded eigen-function belongs. The open intervals*

$$(\lambda_1, \lambda_2), \ (\lambda_3, \lambda_4), \ldots \ (i.e. \ \lambda_1 < \lambda < \lambda_2, \ etc.)$$

consist of eigen-values with the multiplicity $r=2$. The endpoints $\lambda_1, \lambda_2, \ldots$ of the intervals are eigen-values with the multiplicity $r=1$. If an eigen-value interval contains a stationary point λ^*, this is also a double eigen-value and the corresponding eigen-functions are both periodic, with the period p if $f(\lambda^*)$ is a maximum, with the period $2p$ if $f(\lambda^*)$ is a minimum of $f(\lambda)$.

Making use of the fact that the function $v(x)$ which is supposed to be periodic with the period p, has also the period $2p$, Kramers has shown that the last-mentioned case actually occurs. If A is the period matrix of a basis $\varphi(x)$ for the period p, then A^2 is the period matrix of $\varphi(x)$ for the period $2p$. The trace then is

$$f_2 = \operatorname{tr} A^2 = (a_1^{\ 1})^2 + 2a_1^{\ 2}a_2^{\ 1} + (a_2^{\ 2})^2$$
$$= (a_1^{\ 1} + a_2^{\ 2})^2 - 2|A| = f^2 - 2$$

whence we see that

$$f_2(\lambda_0) = -2 \quad \text{if } f(\lambda_0) = 0.$$

Each of the original eigen-value intervals is thus divided in two parts by one of

its points, viz. λ_0, i.e. the zero point of $f(\lambda)$ in this interval (cf. Fig. 2). Evidently λ_0 is a minimum point for $f_2(\lambda)$. In fact

$$\dot{f}_2(\lambda_0)=2f(\lambda_0)\cdot\dot{f}(\lambda_0)=0,\quad \ddot{f}_2(\lambda_0)=2\dot{f}(\lambda_0)^2>0.$$

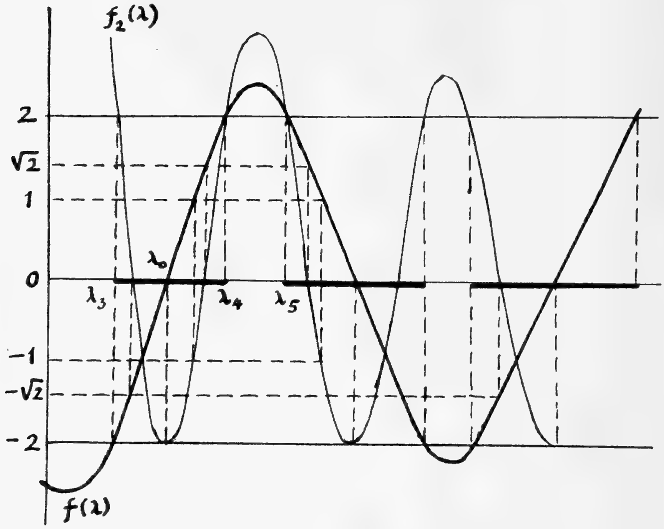

Fig. 2.

Another illustration of this case is given by the function $f_0(\lambda)$ of (5, 2) where all maxima are equal to 2, all minima equal to -2.

6. Periodic Solutions.

By the considerations of section 3 the question as to the periodic solutions of (3, 1) is also decided. The result is that the general solution is periodic with the period kp if and only if the period matrix has the character $\alpha_0=0$ and k-th roots of unity as characteristic roots. Since the characteristic roots of a two-rowed real matrix have to satisfy a real quadratic equation, only 2, 3, 4 are possible values of k, and

if $k=2$, one has $f=\pm 2$
,, $k=3$,, $f=-1$
,, $k=4$,, $f=0$.

The equation (3, 1) has one and only one periodic solution if the character of A is $\alpha_0=1$.

Appendix.

7. Proof of Theorem I.

Without relation to the notations employed in the preceding text, let[6]

$$T=\begin{pmatrix} x_1 & x_2 \\ y_1 & y_2 \end{pmatrix}=\begin{pmatrix} x' \\ y' \end{pmatrix}$$

the regular (real or complex) transformation matrix. It has to satisfy the relation

$$TA=\tilde{A}T$$

[6] In this section the $'$ is used only to indicate transposition of columns and square matrices.

which for the first row $x'=(x_1x_2)$ of T involves the condition

$$x'A=\alpha_1 x',$$

or, by transposition, for the column $x=\begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$:

$$A'x=\alpha_1 x$$

which means that α_1 has to be a characteristic root[7] of the matrix A' (i.e. of A) and x the corresponding " eigen-vector " of A'. If now we choose any column $y=\begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$ that is not linearly dependent on x, e.g. such that the determinant

(7, 1) $$|T|=x_1y_2-x_2y_1=1,$$

we obtain a matrix T satisfying the first condition of the theorem, viz.

$$TAT^{-1}=\begin{bmatrix} x_1 & x_2 \\ y_1 & y_2 \end{bmatrix}\begin{bmatrix} a_1^{\ 1} & a_1^{\ 2} \\ a_2^{\ 1} & a_2^{\ 2} \end{bmatrix}\begin{bmatrix} y_2 & -x_2 \\ -y_1 & x_1 \end{bmatrix}=\begin{bmatrix} \alpha_1 & 0 \\ \alpha_0 & \alpha_2 \end{bmatrix}$$

where

(7, 2) $$\alpha_0=-a_1^{\ 2}(y_1)^2+(a_1^{\ 1}-a_2^{\ 2})y_1y_2+a_2^{\ 1}(y_2)^2.$$

(*a*) If $\alpha_1\neq\alpha_2$ one can choose y as eigen-vector of A' for the root α_2:

$$A'y=\alpha_2 y.$$

Then x, y are certainly linearly independent and

$$TAT^{-1}=\begin{bmatrix} \alpha_1 x_1 & \alpha^1 x_2 \\ \alpha_2 y_1 & \alpha_2 y_2 \end{bmatrix}\begin{bmatrix} y_2 & -x_2 \\ -y_1 & x_1 \end{bmatrix}=\begin{bmatrix} \alpha_1 & 0 \\ 0 & \alpha_2 \end{bmatrix}.$$

If A is symmetric, the discriminant of its characteristic equation is

$$(a_1^{\ 1}+a_2^{\ 2})^2-4(a_1^{\ 1}a_2^{\ 2}-a_1^{\ 2}a_2^{\ 1})=(a_1^{\ 1}-a_2^{\ 2})^2+4(a_1^{\ 2})^2;$$

this disappears if the roots are equal, hence

$$a_1^{\ 1}=a_2^{\ 2},\quad a_1^{\ 2}=0.$$

(*b*) If A is not symmetric and $\alpha_1=\alpha_2$, then this root α_1 is real and one can assume the matrix A in the form $\begin{bmatrix} \alpha_1 & 0 \\ \alpha_0 & \alpha_1 \end{bmatrix}$ where $\alpha_0\neq 0$. In this case the equation $A'x=\alpha_1 x$ means that $\alpha_1x_1+\alpha_0x_2=\alpha_1x_1$, and therefore $x_2=0$. On the other hand the matrix TAT^{-1} should still have 0 in its right upper corner; thus by (7, 2) its left lower element must be $\alpha_0 y_2^{\ 2}$. This is zero only if $y_2=0$. Then, however, the two columns x, y are linearly dependent, and (7, 1) cannot be satisfied. But the condition $\alpha_0y_2^{\ 2}=1$ can be realized, by a real y_2 if $\alpha_0>0$, by a pure imaginary y_2 if $\alpha_0<0$.

It may be pointed out that in the case (*b*) there is one and only one linearly independent eigen-vector of A', while in the case (*a*) there are always two eigen vectors.

Note.—The theorem which is a special case in the theory of elementary divisors is proved here for the convenience of a reader who is not acquainted with this part of linear algebra.

8. Asymptotical Representation of the Eigen-Functions.

We shall prove here the fact used at the beginning of section 5, by integration of the equation (3, 1) by means of the method of successive approximations (cf. Courant-Hilbert, 1924 or 1931*a*; Weyl, 1931*b*). As initial function for the

[7] In fact $|\alpha E-A'|=0$ is necessary and sufficient for the equation $A'x-\alpha x=0$ to have a non-zero solution x.

iterative process we take the solution $\varphi_0(x)$ of (5, 1). Let $\varphi(x)$ be the solution of (3, 1) for the same set of initial values :

$$\varphi(0)=\varphi_0(0)=\begin{bmatrix}1\\0\end{bmatrix},\ \varphi'(0)=\varphi_0'(0)=\begin{bmatrix}0\\1\end{bmatrix}.$$

We put $\varphi(x)$ in the form

$$\varphi(x)=\varphi_0(x)+\varphi^{(1)}(x)+\varphi^{(2)}(x)+\ldots$$

If we determine the function $\varphi^{(n)}(x)$ as solution of the non-homogeneous linear differential equation

(8, 1) $$\frac{d^2y}{dx^2}+\lambda y=v(x)\,.\,\varphi^{(n-1)}(x)\quad (n)=1,\ 2,\ldots)$$

for the initial conditions

$$\varphi^{(n)}(0)=0,\quad \varphi^{(n)\prime}(0)=0$$

and if we write $\varphi^{(0)}(x)=\varphi_0(x)$, it is readily shown that, if the convergence of the process for a certain x-interval is taken for granted, that

$$\varphi''(x)=-\lambda\varphi(x)+v(x)\,.\,\varphi(x)\,;$$

thus (3, 1) is satisfied.

Now we apply again the formula (4, 3)′ by which we obtain the desired solution of (8, 1) in the form

$$\varphi^{(n)}(x)=-\int_{t=0}^{x}\begin{vmatrix}\varphi_{01}(x) & \varphi_{01}(t)\\ \varphi_{02}(x) & \varphi_{02}(t)\end{vmatrix}v(t)\varphi^{(n-1)}(t)dt.$$

If we restrict our discussion to positive values of λ, we get in real terms

$$\varphi^{(n)}(x)=\frac{1}{\sqrt{\lambda}}\int_{o}^{x}\sin\ (\sqrt{\lambda}(x-t))v(t)\varphi^{(n-1)}(t)dt$$

and therefore

(8, 2) $$\varphi(x)=\varphi_0(x)+\frac{1}{\sqrt{\lambda}}\int_{o}^{x}\sin\ (\sqrt{\lambda}(x-t))v(t)\varphi(t)dt.$$

With regard to (4, 2) it will be sufficient to estimate the integral on the right-hand side of (8, 2) for $x=p$. We have

$$\left|\int_{o}^{p}\sin\ (\sqrt{\lambda}(p-t))v(t)\varphi_j(t)dt\right|<\int_{o}^{p}|v(t)||\varphi_j(t)|dt$$

which because of the Cauchy-Schwarz inequality is

$$\leqslant\sqrt{\int_{o}^{p}v(t)^2dt\,.\int_{o}^{p}\varphi_j(t)^2dt}=M$$

where M is a certain positive constant. Therefore

(8, 3) $$|\varphi_j(p)-\varphi_{0j}(p)|<\frac{M}{\sqrt{\lambda}}.$$

By differentiation we get from (8, 2)

$$\varphi'(x)=\varphi_0'(x)+\int_{o}^{x}\cos\ (\sqrt{\lambda}(x-t))v(t)\varphi(t)dt.$$

In order to estimate this integral we apply to it an integration by parts; in this way it appears as a difference of two bounded terms, each divided by $\sqrt{\lambda}$; thus there is also a fixed positive M_1 such that

$$|\varphi_j'(p)-\varphi'_{0j}(p)|<\frac{M_1}{\sqrt{\lambda}}. \tag{8, 4}$$

If $v(x)$ has no continuous derivative, integration by parts cannot be applied here. That the result is still true under the more general suppositions made in section 3, follows from Riemann's lemma (cf. Whittaker-Watson, 1927*b*). Hence it also follows that in the inequality (8, 3), but not in (8, 4), the denominator $\sqrt{\lambda}$ may be replaced by λ.

Summary.

After a few introductory remarks on boundary- and eigen-value- problems in modern physics the eigen-value problem of the one-dimensional Schroedinger equation with periodic coefficient (Hill's equation), for bounded eigen-functions, is treated in a direct way after the method of Kramers. In section 3 Floquet's theory is presented as a consequence of the theory of elementary divisors for the period matrix, in a form which suggests generalization. In sections 4 and 5 the eigen-value intervals are determined through a discussion of the similarity invariants of the period matrix. In section 6 all periodic eigen-functions are established.

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The University of Adelaide,
South Australia.

EVAPORATION OF OXYGEN FROM A TUNGSTEN SURFACE.

By R. C. L. Bosworth, Ph.D., D.Sc.

Manuscript Received, October 22, 1945. Read December 5, 1945.

An experimental determination of the rate of evaporation of oxygen on tungsten films was recorded in 1937 by Bosworth and Rideal (1937). The method of contact potentials was used and the rate of drift of the surface potential was followed when the temperature of the wire carrying the oxygen film was held steady at a number of points giving measurable rates of evaporation. These temperatures varied from 1270° K. to 1930° K. From the resultant surface potential versus time curves at constant temperature, derived rate of change of surface potential versus temperature at constant surface potential curves were drawn. Using the Clausius-Clapeyron equation, a series of values of the heat of evaporation at a number of fixed values of the surface potential were then computed from the second family of curves. Tables of such figures are given in the paper referred to above.

From the study of condensation of oxygen on tungsten the variation of the surface potential with the fraction (θ) of the surface covered has recently been given (Bosworth, 1945*a*), so that we are now in a position to give the heat of evaporation as a function of θ. The resultant relationship is shown in graphical form in Figure 1. It will be observed that the figure is no longer symmetrical about the ordinate $\theta=0\cdot5$ as predicted by the theory of evaporation of diatomic molecules as proposed by Roberts (1939) and as found in the case of nitrogen on tungsten films (Bosworth, 1945*b*).

Spreading Forces in Oxygen on Tungsten Films.

Reference to Figure 1 shows that the molar heat of evaporation (E) of oxygen from a nearly bare tungsten surface is 154 kilogram calories per gram molecule and that this quantity decreases approximately linearly with increase in θ to a value of 82 kilocalories per gram molecule at $\theta=0\cdot5$. About this point E begins to vary less rapidly, and at $\theta=1\cdot0$ has fallen only to 66 kilocalories per gram molecule.

The functional relationship between E and θ is related to the surface spreading force F, or the free energy per unit area possessed by the surface in virtue of the intermolecular interaction in the film. The most important thermodynamical equation involving F and the properties of the bulk phase is given by the Gibb's adsorption isotherm :

$$dF=\sigma \mathbf{R}T\ d\ln p_{\mathrm{a}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where σ is the number of adsorbed gram atoms present on the surface, $\mathbf{R}$ is the (molar) gas constant, T the absolute temperature and p_{a} is the partial pressure due to atoms in the gas phase. Since the act of dissociation involves the chemical reaction,

$$O_2=2\ O$$

we have for the partial pressure of molecules p_{m},

$$p_{\mathrm{m}}=k\ p_{\mathrm{a}}^2,$$

where k is the appropriate reaction constant. Since the equilibrium between oxygen atoms and molecules at ordinary temperatures is so far over

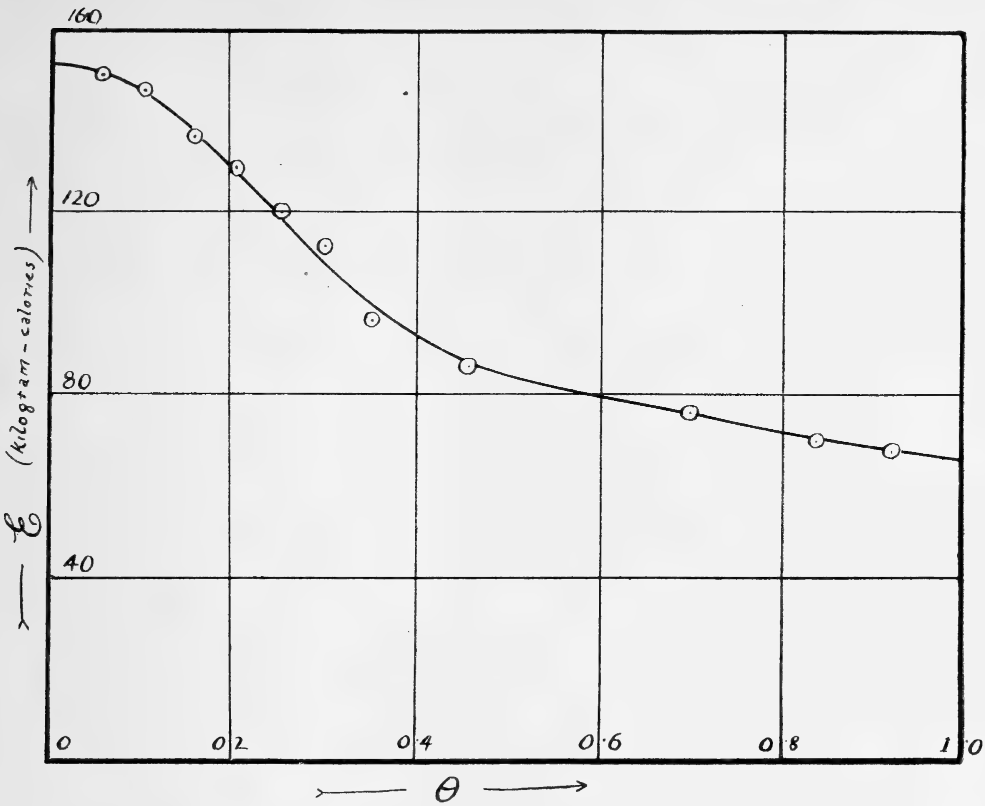


Fig. 1.

towards the molecular state the total pressure p differs from the partial pressure p_m due to molecules by an infinitesimal amount. We therefore can write :

$$d \ln p_a = \tfrac{1}{2} d \ln p.$$

Equation (1) now becomes :

$$dF = \tfrac{1}{2}\sigma \mathbf{R}T \; d \ln p. \qquad (2)$$

The relationship between the pressure p in equilibrium with a film at temperature T is expressed by the well-known latent heat equation

$$\ln p = -\frac{\mathsf{E}}{\mathbf{R}T} + \frac{dT}{\mathbf{R}T^2}(C_p - C_{p(sol)}) + \mathrm{i}.$$

where C_p is the specific heat of the gas phase,
$C_{p\ sol}$ the specific heat of the adsorbed phase, and
i is the appropriate vapour pressure constant.

Since it has been shown that $\mathsf{E} >> \mathbf{R}T$ the specific heat terms in the equation above may be ignored and the equation taken as :

$$\ln p = -\frac{\mathsf{E}}{\mathbf{R}T} + \mathrm{i}', \qquad (3)$$

or $\mathbf{R}T \, d \ln p = -d\mathsf{E}$. (3a)

On substituting equation (3a) in equation (2), we obtain

$$dF = -\tfrac{1}{2}\sigma d\mathsf{E},$$

or

$$F = -\tfrac{1}{2}\int \sigma d\mathsf{E}. \qquad (4)$$

On performing a graphical integration in terms of the data shown in Figure 1 values of F given in Table I were computed.

TABLE I.

Spreading Forces in Oxygen on Tungsten Films Calculated from Heats of Evaporation.

F Spreading Force in dynes per cm.	θ Fraction of Surface Covered.
32	0·10
135	0·20
580	0·40
1,330	0·60
2,100	0·80
2,880	1·00

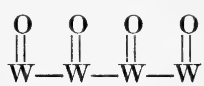
The magnitude of these spreading forces is particularly impressive. In the complete film the spreading force is about a hundred times larger than that commonly experienced in liquid substrates.

Over the range from $\theta=0 \cdot 4$ to $\theta=1 \cdot 0$, F increases almost proportionally to θ; i.e. the extra surface energy increases proportionally to the surface population, each additional adsorbed atom is contributing a definite amount to the surface free energy.

Discussion on the Chemical Structure of Oxygen on Tungsten Films.

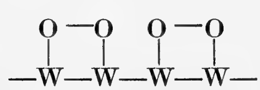
There are three possible chemical structures which could be assigned to the oxygen on tungsten films:

(*a*)



(*b*)

(*c*)



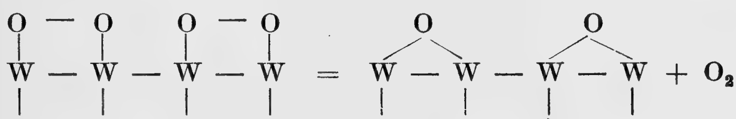
In each of these three structures there are just as many oxygen atoms as tungsten atoms on the surface. Formulæ (*a*) and (*b*) presuppose that the tungsten surface atoms are divalent, formula (*c*) that they are monovalent. Now Roberts (1935) has shown that one molecule of oxygen is capable of replacing one molecule of hydrogen on a tungsten surface. It would seem therefore that formula (*c*) is most likely to be the true one. In terms of this formula we may regard the oxygen film as that of a surface peroxide. The structure of the hydrogen peroxide molecule has been derived by Penny and Sutherland (1934). The molecule is an unsymmetrical one in which the OH bonds each of length 1·0 Å. make an angle of 110° with the OO bond of length 1·4 Å. The OH

bonds are skew and make an angle of 100° with one another. The distance between the two H atoms is therefore

$$\{(1\cdot 4+2\sin 20)^2+(1\cdot 0\cos 20+\sin 10)^2+(1\cdot 0\cos 20)^2\}^{\frac{1}{2}}\text{ Å.},$$
$$=2\cdot 6\text{ Å.}$$

According to Davey (1925) tungsten crystallises in a body centred cube of side $3\cdot 155$ Å. The nearest neighbours on the 110 plane therefore have a spacing of $\sqrt{\frac{3}{2}}\times 3\cdot 155=2\cdot 73$ Å. The peroxide structure could therefore fit nicely on to the two nearest neighbours on a tungsten surface with very little distortion of the valence angles and we get a surface compound in which two oxygen atoms are tied to two lattice points.

The proposed peroxide structure would indicate that any film of surface concentration greater than $\theta=0\cdot 5$ is in a sense a saturated film in that there are no free chemical valences on the surface. The bonds set free by the loss of any two oxygen atoms from the surface could easily be taken up by a peroxide group splitting into two oxide atoms each bound to the surface through two separate tungsten atoms, viz.:



(1) (2)

Since the oxygen bonds of compound are distorted more than those of compound (1), we must regard the latter as less stable.

The chemical equation above represents a surface peroxide ($\theta=1\cdot 0$) changing over to a surface oxide ($\theta=0\cdot 5$) with loss of half the adsorbed oxygen but with retention of the saturated character of the tungsten valences and may perhaps explain in part why the heat of evaporation varies so little between $\theta=0\cdot 5$ and $\theta=1\cdot 0$.

The Kinetics of the Evaporation of Oxygen.

While Langmuir and Villars (1931) have claimed that oxygen evaporating from hot tungsten consists of isolated atoms and not molecules their argument appears to apply only to very dilute films. Roberts (1936) indeed has shown that this view is inconsistent with his formula for the time required for evaporation as a function of temperature. Further, the figures given above for the heat of evaporation as a function of θ are inconsistent with the hypothesis of evaporation of atoms except possibly for films more dilute than $\theta=0\cdot 2$.

The heat of dissociation of oxygen in the gas phase is known to be 117 kilocalories per gram molecule. If E is the heat of desorption at a concentration σ, and if E' is the corresponding heat of adsorption at the same surface concentration, then evaporation in the form of atoms is energetically possible only provided that

$$2\mathsf{E}-\mathsf{E}'>117.$$

For films of "half value" Roberts has found a value of 139 kilocalories per gram molecule for E'. E must therefore have a value of at least 128 kilocalories in order that the tungsten should produce dissociation of the oxygen, and this we see from Figure 1 above is only possible for films more dilute than $\theta=0\cdot 2$. For all more concentrated films the oxygen must evaporate largely in the molecular form.

In a concentrated film every adsorbed atom is associated with a near neighbour and thus may readily evaporate as a molecule. When, however, the

film is more dilute than about $\theta = 0 \cdot 5$ there are very few paired atoms left on the surface, so that the rate of molecular evaporation falls off rapidly and now is regulated by the rate at which separate oxygen atoms can move together to form a pair on neighbouring lattice points, i.e. a peroxide linkage. In other words evaporation at low surface concentrations is controlled by surface migration. At first sight this appears rather a strange statement as the activation energy for a surface diffusion process must always be less than the heat of evaporation if surface migration is to be observed at all. It has been pointed out, however, by Bosworth and Rideal (1937) that ordinary surface diffusion is always supplemented by the spreading forces which assist the process of diffusion by lowering the activation energy. In oxygen films we have shown that these spreading forces are particularly large and must practically dominate the process of surface diffusion. Ordinarily one studies the process of surface diffusion down the gradient of surface concentration and down the gradient of the spreading force so that the spreading force is assisting the diffusion. In the case in hand, however, the diffusion required to bring two atoms together on the surface must act against the gradient of the spreading force and consequently should require a higher activation energy than normal migration and could conceivably control the rate of evaporation. Furthermore this diffusion against the gradient of the concentration requires the breaking of surface bonds by the change over from two oxide linkages to one peroxide linkage and two holes, viz. :

a reaction which would also appear to require an expenditure of energy.

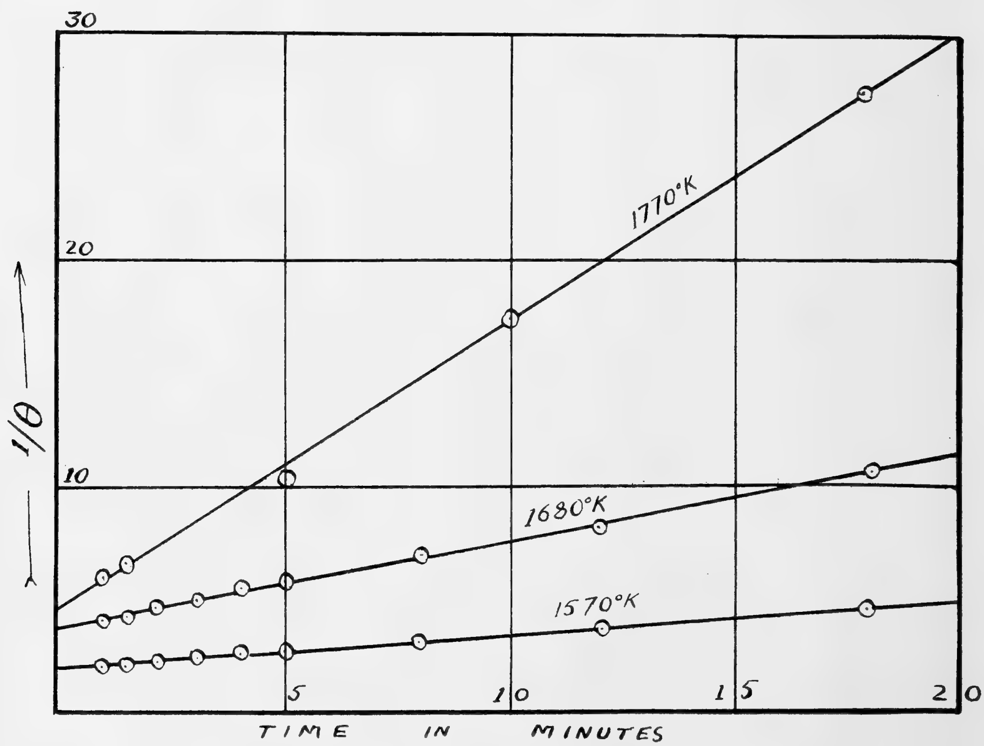


Fig. 2.

If this mechanism for the evaporation is correct it would indicate that the evaporation process for a dilute film should follow approximately a bimolecular law. Figure 2 shows $1/\theta$ plotted as a function of the time. The points obtained at the temperatures studied are satisfactorily collinear. This may be taken as further evidence that, under the conditions studied, oxygen evaporates from the surface as molecules and not as atoms.

Summary.

From measurements of the rate of change of the contact potential of a tungsten surface, covered with an oxygen film and heated to a temperature at which that film becomes volatile, the heat of evaporation of oxygen from tungsten is calculated as a function of the fraction of the surface covered. From the resultant figures the surface spreading forces have been derived. For a complete film the spreading force amounts to 2,880 dynes per cm.

Since it has been shown by Roberts that one molecule of oxygen replaces one of hydrogen on a tungsten surface it is proposed that the surface structure representing a complete film of oxygen should be that of a peroxide, while the surface which is just half saturated has the structure of the corresponding surface oxide. This arrangement would account for the relatively small change in the heat of evaporation as the surface concentration changes from $\theta=0 \cdot 5$ to $\theta=1 \cdot 0$.

Evaporation of molecular oxygen from a dilute film on a tungsten surface involves primary surface migration against the gradient of the spreading force and kinetically the reaction is bimolecular.

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ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 4th, 1945.

The Annual Meeting, being the six hundred and twenty-first General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Seventy-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

A. BOLLIGER, Ph.D., A.A.C.I.

Vice-Presidents :

G. D. OSBORNE, D.Sc., Ph.D.
A. B. WALKOM, D.Sc.
PROF. H. PRIESTLEY, M.D., Ch.M., B.Sc.
F. LIONS, B.Sc., Ph.D., A.R.I.C.

Hon. Secretaries :

PROF. A. P. ELKIN, M.A., Ph.D.
D. P. MELLOR, D.Sc.

Hon. Treasurer :

A. CLUNIES ROSS, B.Sc., F.C.A. (*Aust.*).

Members of Council:

A. ALBERT, Ph.D., B.Sc., A.R.I.C.
R. L. ASTON, B.E., M.Sc., Ph.D., A.M.I.E. (*Aust.*).
J. A. DULHUNTY, D.Sc.
F. P. J. DWYER, D.Sc.
H. O. FLETCHER.
A. MACCOLL, M.Sc.
F. R. MORRISON, A.A.C.I., F.C.S.
R. S. NYHOLM, M.Sc.
H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and, on the recommendation of Mr. A. Clunies Ross, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1945.

1944.	LIABILITIES.	1945.					
£		£	s.	d.	£	s.	d.
35	Accrued Expenses				126	1	6
9	Subscriptions Paid in Advance				15	4	6
81	Life Members' Subscriptions—Amount carried forward				81	0	0
	Trust and Research Funds (detailed below)—						
1,834	Clarke Memorial	1,854	16	5			
726	Walter Burfitt Prize	1,051	10	0			
726	Liversidge Bequest..	700	0	0			
3,049	Research	3,148	10	0			
					6,754	16	5
25,398	ACCUMULATED FUNDS				25,707	11	11
(902)	Contingent Liability—In connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d.						
£31,858					£32,684	14	4

1944.		ASSETS.	1945.					
£	£		£	s.	d.	£	s.	d.
	451	Cash at Bank and in Hand				926	4	4
		Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—						
		Held for—						
		Clarke Memorial Fund	1,800	0	0			
		Walter Burfitt Prize Fund	700	0	0			
		Liversidge Bequest..	700	0	0			
		Research Fund	3,000	0	0			
		General Purposes	3,560	0	0			
	9,360					9,760	0	0
	29	Prepayment				—		
101		Debtors for Subscriptions	46	4	0			
101		*Deduct* Reserve for Bad Debts	46	4	0			
—	—					—		
	14,756	Science House—one-third Capital Cost				14,756	0	0
	6,800	Library—At Valuation				6,800	0	0
	414	Furniture—At Cost—*less* Depreciation				397	0	0
	35	Pictures—At Cost—*less* Depreciation				33	10	0
	13	Lantern—At Cost—*less* Depreciation				12	0	0
	£31,858					£32,684	14	4

TRUST AND RESEARCH FUNDS.

	Clarke Memorial.	Walter Burfitt Prize.	Liversidge Bequest.	Research.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Capital at 29th February, 1944	1,800 0 0	700 0 0	700 0 0	3,000 0 0
Add Donation, January, 1945	—	300 0 0	—	—
	£1,800 0 0	£1,000 0 0	£700 0 0	£3,000 0 0
Revenue—				
Balance at 29th February, 1944	34 4 7	25 15 0	25 15 0	49 5 0
Interest for twelve months	65 10 2	25 15 0	25 15 0	99 5 0
From General Funds ..	—	—	0 11 7	—
	99 14 9	51 10 0	52 1 7	148 10 0
Deduct Expenditure ..	44 18 4	—	52 1 7	—
Balance at 28th February, 1945 ..	£54 16 5	£51 10 0	—	£148 10 0

ACCUMULATED FUNDS.

	£ s. d.
Balance at 29th February, 1944	25,397 11 11
Add Reduction of Reserve for Bad Debts ..	5 5 0
Add Surplus for twelve months (as shown by Income and Expenditure Account) ..	304 15 0
	£25,707 11 11

A. CLUNIES ROSS,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1945, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 21st March, 1945.

INCOME AND EXPENDITURE ACCOUNT.
1st March, 1944, to 28th February, 1945.

1943-4. £		1944-5. £	s.	d.	£	s.	d.
412	To Printing and Binding Journal—Vol. 77	307	19	2			
303	,, Salaries	310	5	0			
117	,, Library—Purchases and Binding	29	18	11			
73	,, Printing—General	113	10	5			
55	,, Miscellaneous	63	0	0			
54	,, Postage and Telegrams	66	2	3			
43	,, Rent—Science House Management Committee	46	15	8			
36	,, Cleaning	34	0	0			
25	,, Depreciation	23	18	0			
18	,, Telephone	18	12	4			
15	,, Insurance	15	0	2			
13	,, Audit	12	12	0			
11	,, Electricity	9	6	3			
5	,, Repairs	1	8	9			
1,180					1,052	8	11
113	,, Surplus for Twelve Months				304	15	0
£1,293					£1,357	3	11

1943-4. £		1944-5. £	s.	d.	£	s.	d.
470	By Membership Subscriptions				459	7	6
400	,, Government Subsidy				400	0	0
300	,, Science House—Share of Surplus				360	0	0
106	,, Interest on General Investments				120	3	6
	,, Receipts from Reprints	37	8	0			
	Less Expenditure	22	15	7			
4					14	12	5
2	,, Other Receipts				3	0	6
11	,, Proportion of Life Members' Subscriptions				—		
£1,293					£1,357	3	11

The Annual Report of the Council (1944-45) was read, and on the recommendation of Professor Elkin, adopted.

Report of the Council, 1944-1945 (Rule XXVI).

We regret to report the loss by death of two members since April 1st, 1944 : Norman Dawson Royle (1929), Charles Anderson (1905), also of an honorary member, Thomas Ranken Lyle (1931).

By resignation the Society has lost two members : A. J. Robinson and A. P. Penman.

The names of five members have been removed from the register and their arrears have been written off.

The membership now stands at 291, twelve new members having been elected during the year, namely, Alwynne Drysdale Bennett, Daniel George Moye, Colin Lachlan Adamson, George William Kenneth Cavill, Cyril Maxwell Martin, Andrew David Thomas, Hugh Albert McKenzie, William Hamilton Watkins, Harry Warner, John Charles Erhart, James Alan Friend and John Bryan Willis.

Eleven ordinary meetings of the Council and one special meeting were held during the year beginning April 1st, 1944, at which the average attendance was 14. During the same period nine general monthly meetings were held, with an average attendance of 42 members.

Twenty-eight papers were accepted for reading and publication during the year, and the following short talks were given :

"Potential Topography in Electronics", by Dr. A. L. Reimann.
"Physical Aspects of Vision", by R. G. Giovanelli, M.Sc.
"Approximations", by H. H. Thorne, M.A., B.Sc.
"Some Aspects of Physiological Black-out in Aviation", by Professor F. S. Cotton, D.Sc.
"Some Aspects of Settlement in the Ord River District, North-West Australia", by W. H. Maze, M.Sc.
"The Chemical Attack on Tuberculosis", by Dr. F. Lions.
"Some Post-War Problems of New Guinea", by Brig.-Gen. Sir Walter McNicoll and Professor A. P. Elkin.

Exhibits.—" Fluorescence of Animal Skins, with particular reference to *Trichosurus vulpecula* ", by Dr. A. Bolliger; " A Powerful Permanent and Transmuted Wood Magnet in Alnico "; and " The Streaming Double Refraction of the Tobacco Mosaic Virus ", by Dr. D. P. Mellor, were given during the year.

Lecture.—A lecture, entitled " The Evolution of Surveying Instruments ", was given by Dr. R. L. Aston.

Film.—A sound colour film, " Crystals Go to War ", was shown.

Symposium.—At the monthly meeting in August, a symposium, " Trace Elements Essential to Life ", was held, the following being the subjects and speakers :

" Trace Elements in the Soil ", by Dr. E. G. Hallsworth.

" Trace Elements in Plants ", by Professor E. Ashby.

" Trace Elements in Biochemistry ", by Dr. J. L. Still.

Great interest was shown in the subject and one hundred and twelve members and visitors were present, a number of whom took part in the discussion which followed the addresses.

Exhibition of Photographs and President's " At Home ".—With the object of bringing members together, the President arranged an Exhibition of Photographs of Scientific Interest, which was held on Saturday, November 25th, 1944, at David Jones' Small Art Gallery. The meeting was a great success, and members expressed the hope that another function of this kind would soon be held.

Popular Science Lectures.—Five Popular Science Lectures were given during the months June-October inclusive, and were well attended by the general public and by members of the Society.

June 15th.—" Man and Heredity ", by A. N. Colefax, B.Sc.

July 20th.—" Fuels in the Service of Man ", by J. A. Dulhunty, B.Sc.

August 17th.—" Man and Metals ", by F. P. J. Dwyer, M.Sc.

September 21st.—" Man and the Expanding Universe ", by Father D. J. K. O'Connell, S.J., M.Sc., F.R.A.S.

October 19th.—" My Lady's Perfume ", by F. R. Morrison, A.A.C.I., F.C.S.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1944 was given by Dr. W. H. Bryan, M.C., D.Sc., on May 30th, the title being " An Australian Geologist Looks at the Pacific ".

Clarke Memorial Medal.—The Clarke Memorial Medal for 1944 was awarded to Professor W. E. Agar of the University of Melbourne for his researches in zoology.

Walter Burfitt Prize.—The Walter Burfitt Prize for 1944 was awarded to Dr Hereward Leighton Kesteven, D.Sc., M.D., of Sydney, for his outstanding published work in related fields of osteology, embryology and anatomy of vertebrates during the three years ended December 31st, 1943.

The capital of this fund has been augmented by £300 through the kind generosity of Mrs. E. E. Burfitt, the fund now standing at £1,000.

Liversidge Lectures.—The Liversidge Lectures were delivered by Dr. F. P. Bowden on Tuesday and Wednesday, October 17th and 18th, 1944, on " The Physics of Rubbing Surfaces ".

Patron of Society.—H.R.H. the Duke of Gloucester, Governor General of Australia, has kindly consented to become Patron of the Society. On Monday, March 12th, 1945, an Address of Welcome was presented to H.R.H. on behalf of the Society, by the President (Dr. G. D. Osborne) and Honorary Secretaries (Professor A. P. Elkin and Dr. D. P. Mellor).

Government Grant.—A grant of £400 was received from the Government of New South Wales, whose continued interest in the Society's work is much appreciated.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition. During the year £400 has been invested in war loans, and a further £200 has been converted.

Payment of Popular Science Lecturers.—It was decided that in future Popular Science Lecturers, if not members of Council, should be paid £3 3s. a lecture.

Financial Assistance to Authors.—It was decided that financial members contributing papers to the *Journal and Proceedings* should be paid the sum of five shillings per printed journal page. The total sum paid, however, shall not exceed £3 for any one paper, nor £10 in any one year, this sum to be payable from the Research Fund of the Society. This plan is to be adopted for one year, commencing April 1st, 1945.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1944, to February 28th, 1945, has been £360. During the year storage cubicles have been erected. The Royal Society's share of the cost of these was £50.

Owing to the fact that National Security Regulations have been relaxed, the glass has been restored to the doors of the Society's office and reception room.

Science House Management Committee.—The Royal Society has been represented at meetings of the Management Committee of Science House by Mr. A. R. Penfold and Dr. G. D. Osborne, with Mr. Alan Clunies Ross and Dr. F. Lions as substitute representatives. Mr. Penfold submitted his resignation in January, as he would be absent overseas for some time on a Government Mission. No one has yet been appointed in his place.

The Library.—The amount of £29 11s. 2d. has been expended on the purchase of periodicals, and the amount of £34 13s. is being spent on binding ; in addition, the amount of £3 13s. was spent on the duplication of the library list of exchanges ; the amount expended on the library will therefore be £67 17s. 2d.

Exchanges.—The number of volumes now being sent to other societies is 233.

Accessions.—For the twelve months ended in February the number of accessions entered in the catalogue was 1,206 parts of periodicals, and 43 whole volumes.

Borrowers and Readers.—Members and visitors reading in the library numbered 23.

The number of books and periodicals borrowed by members, institutions and accredited readers was 170.

Among the institutions which made use of the arrangements for inter-library borrowing were : McMaster Animal Health Laboratory, University of Sydney, National Standards—Radiophysics Library, Allied Geographical Section, C.S.I.R., Melbourne, Sydney County Council Library, University of Queensland, Commonwealth Library, C.S.I.R., Canberra, The Australian Museum, Peters Ice Cream Co., Royal North Shore Hospital, and Commonwealth Solar Observatory.

New Edition of Pitt's Catalogue.—At the request of the C.S. and I.R., Melbourne, all holdings in the Royal Society's library are being checked for inclusion in a new edition of Pitt's Catalogue of Scientific Periodicals in the Australian Libraries.

Duplication in the Libraries of Science House.—It has been decided to carry on with the suggestion for saving shelving space in the library by making the library of the Linnean Society of New South Wales and the Royal Society's library complementary.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Frederick William Ayscough, Norma Dorothy Laing and Barbara Wright.

Patron of Society.—It was announced that H.R.H. the Duke of Gloucester had granted his patronage to the Society.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1945 to Professor W. N. Benson.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1945 would be delivered by Professor E. S. Hills on June 13th, the title of the lecture being " Some Aspects of the Tectonics of Australia "

Walter Burfitt Prize.—The Walter Burfitt Prize for 1944 was presented to Dr. H. L. Kesteven.

William James Farrer Centenary.—It was announced that the William James Farrer Centenary fell on April 3rd, 1945. The suggestion by Dr. R. J. Noble that his work should be made the subject for a lecturette was adopted.

Election of Auditors.—On the motion of Mr. R. W. Challinor, seconded by Dr. H. S. H. Wardlaw, Messrs. Horley and Horley were re-elected as Auditors to the Society for 1945-46.

Library.—The following donations were received : 403 parts of periodicals, 12 whole volumes and seven back numbers.

Correspondence.—Letter from Professor J. Neill Greenwood calling attention to the proposed symposium on the Failure of Metals by Fatigue was read. Also notices of a public meeting and conference on Soil Erosion and Water Conservation were distributed to members.

The President, Dr. G. D. Osborne, delivered his address, entitled " Some Recent Trends in Geological Science and the Outlook on Some of its Frontiers ".

Dr. G. D. Osborne then installed Dr. A. Bolliger as President for the year 1945-46. Dr. Bolliger expressed his appreciation of the honour conferred on him. He then called on Mr. C. A. Sussmilch to move a vote of thanks to the retiring President for his valuable address and for his work for the Society during the past year. This was carried with acclamation.

The following paper was read by title only : " General Geology of the Wellington District, N.S.W.", by E. M. Basnett, M.Sc., and M. J. Colditz, B.Sc.

May 2nd, 1945.

The six hundred and twenty-second General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Professor H. Priestley, was in the chair. Forty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Dr. Edward Sutherland Stokes, a member since 1909.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Harold Burnell Carter, Leonard Luber, Lyndon Charles Noakes and Jack Lehane Willis.

Library.—The following donations were received: 133 parts of periodicals and four back numbers.

Lecturette.—A lecturette on "Organisation of Science in the United States and its Relationship to Australian Science through a Scientific Liaison Office" was given by Mr. N. A. Whiffen, A.A.C.I.

Exhibit.—Mr. D. P. Mellor gave an exhibit entitled "Transmuted Wood".

June 6th, 1945.

The six hundred and twenty-third General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Forty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Ronald Arthur Eade, John Seymour Proud, Laurence Gordon Walters and Evelyn May Webster.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1945 would be delivered on Wednesday, June 13th, 1945, at 8 p.m., in the Geology Theatre, University of Sydney, by Professor E. S. Hills, D.Sc., Ph.D., the title being "Some Aspects of the Tectonics of Australia".

Popular Science Lecture.—It was also announced that the first Popular Science Lecture for 1945 would be given by R. S. Nyholm, M.Sc., on Thursday, June 21st, at 8 p.m., and would be entitled "The Chemistry of Water and Washing".

Library.—The following donations were received: 126 parts of periodicals, 10 whole numbers and 22 back numbers.

The following papers were read:

"Determination of the Boiling Points of Hydrogen Chloride Solutions", by L. M. Simmons, B.Sc., A.A.C.I. (Communicated by Dr. F. Lions.) This paper was discussed by Dr. H. S. H. Wardlaw and Dr. G. Harker.

"Contact Potential Difference as a Tool in the Study of Adsorption", by R. C. L. Bosworth, Ph.D., D.Sc.

"Radiant Heat Loss as a Problem in Effusion", by R. C. L. Bosworth, Ph.D., D.Sc.

Lecturette.—A lecturette entitled "Aerial Infection" was given by Miss P. M. Rountree, M.Sc., Dip.Bac.

July 4th, 1945.

The six hundred and twenty-fourth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Fifty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Thomas Hodge Smith, a member since 1922.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Arthur Roylance Coombes, Samuel Morris and Alwyn Walker Prescott.

Popular Science Lecture.—It was announced that the second Popular Science Lecture for 1945 would be given by Jean Armytage, M.B., B.Sc., M.R.A.C.P., on Thursday, July 19th, at 8 p.m., the title being "Penicillin and its Medical Uses".

Library.—The following donations were received: 84 parts of periodicals, four whole volumes and six back numbers.

Address.—An address entitled "Indonesia" was given by Mr. J. B. D. Pennink, Consul-General for the Netherlands.

Films.—The following films were shown by courtesy of the Netherlands-Indies Government Information Service :

" Indonesian Harmony."

" Deliveration of the Indies."

August 1, 1945.

The six hundred and twenty-fifth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Dr. G. D. Osborne, was in the chair. Seventy members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death of the following member was announced : Richard Old, a member since 1903.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

Popular Science Lecture.—It was announced that the third Popular Science Lecture for 1945 would be given by F. Lions, B.Sc., Ph.D., A.R.I.C., on Thursday, August 16th, at 8 p.m., and would be entitled " Triumph over Pain : The Story of Anæsthesia ".

Symposium.—The announcement was made that the September monthly meeting would be devoted to a symposium on " Visual Education ", the principal speaker being Squadron-Leader N. Rosenthal.

Library.—The following donations were received : 89 parts of periodicals, four whole volumes and eight back numbers.

The following papers were read by title only :

" Friction between Keratin Surfaces as Affected by Some Shrink-proofing Treatments ", by M. Lipson, B.Sc., A.A.C.I., and P. Howard, B.Sc.

" A Study of the Reflection of Light in the Case of Three Homogeneous, Isotropic, Non-Conducting Media in Successive Contacts ", by J. Bannon, B.Sc., F.Inst.P. (Communicated by Professor V. A. Bailey.)

Symposium.—A symposium was held on " Fluorine ", the subject being introduced by Dr. G. D. Osborne.

In his short address entitled " Inorganic Compounds of Fluorine ", Dr. D. P. Mellor referred to the possible use of uranium hexafluoride in the separation of uranium isotope 235.

Under the heading " Fluorine in Organic Chemistry ", Dr. F. Lions outlined the use of fluorine compound in organic syntheses and made special reference to the synthesis of high octane fuels.

Speaking on " Fluorine in Dental Health ", Dr. N. E. Goldsworthy outlined the role of fluorine in causing mottling of dental enamel and also its effect on the incidence of dental caries.

September 5th, 1945.

The six hundred and twenty-sixth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. One hundred and four members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death of the following member was announced : Frederick Stapleton Mance, a member since 1924.

The President also announced that Brigadier H. B. Taylor, a member of the Society, had been released from a Japanese prisoner-of-war camp.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : Alan Charles Higgs.

Popular Science Lecture.—It was announced that the fourth Popular Science Lecture for 1945 would be given by Professor A. H. McDonald, M.Sc., Ph.D., on Thursday, September 20th, at 8 p.m., and would be entitled " The Mediterranean—Past and Future ".

University Liversidge Lecture, 1945.—It was also announced that the Liversidge Lecture for 1945 would be delivered on Thursday, September 13th, by Professor J. B. Speakman, at 8 p.m., in the Chemistry Department, University of Sydney, the title of the lecture being " The Chemistry of Wool and Related Fibres ".

Library.—The following donations were received : 102 parts of periodicals and 13 whole volumes.

The following paper was read by title only :

" A Convenient Vacuum Method for the Preparation of Nitrogen ", by R. C. L. Bosworth, D.Sc., Ph.D.

Symposium.—The meeting was devoted to a symposium on "Visual Education", the discussion being opened by Squadron-Leader N. Rosenthal, who illustrated his talk with the following films:

"Principles of Radar."

"The Heart and Circulation of the Blood."

"The Electron."

"The Symphony Orchestra."

"Diary of a Sergeant (Medical Rehabilitation)."

Mr. J. C. Storey then gave a short address.

October 3rd, 1945.

The six hundred and twenty-seventh General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Twenty-one members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Professor J. T. Wilson, an honorary member since 1922, and an ordinary member from 1890 to 1921.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Jean Armytage and Phyllis Margaret Rountree.

Popular Science Lecture.—It was announced that the fifth Popular Science Lecture for 1945 would be given by Professor G. G. McDonald, B.Sc., Ph.D., on Thursday, October 18th, at 8 p.m., and would be entitled "Liquid Life".

Library.—The following donations were received: 163 parts of periodicals and 11 whole volumes.

The following papers were read:

"The Vibration Frequencies of the Trigonal Bipyramidal Model AB_3C_2", by A. Maccoll, M.Sc.

"Quaternary Arsonium Salts and their Metallic Co-ordination Compounds. Part III. Cobalt", by F. P. Dwyer, M.Sc., N. A. Gibson, M.Sc., and R. S. Nyholm, M.Sc.

"The Chemistry of Bivalent and Trivalent Rhodium. A Note on the Constitution of Hydrogen-Bisdimethylglyoxime-Dichlororhodate", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

"The Chemistry of Bivalent and Trivalent Iridium. Part III. Complexes of Tertiary Arsines with Trivalent Iridium Halides", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

"Uric Acid Content of Hair, Horn and Feathers", by A. Bolliger, Ph.D.

"Friction between Keratin Surfaces as Affected by some Shrink-proofing Treatments". by M. Lipson, B.Sc., A.A.C.I., and P. Howard, B.Sc.

Lecturette.—A lecturette entitled "Great Telescopes" was given by H. W. Wood, M.Sc., Government Astronomer.

November 7th, 1945.

The six hundred and twenty-eighth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Twenty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected members of the Society: Hellmut Friedrich Furst, Pauline Mary Sambell and Aileen Sampson.

Popular Science Lecture.—It was announced that the Popular Science Lecture entitled "Liquid Life", which was postponed from October 18th, 1945, owing to lack of lighting facilities, would be delivered by Professor G. G. McDonald, B.Sc., Ph.D., on Thursday, November 15th, 1945, at 8 p.m.

Society for Experimental Biology of N.S.W.—It was also announced that the Society for Experimental Biology would hold a meeting on Tuesday, November 20th, 1945, at 7 p.m., in the Veterinary Science School, University of Sydney. The subject of discussion would be "Fluorine—Some Biological Aspects".

Library.—The following donations were received: 130 parts of periodicals and two whole volumes.

The following papers were read:

"Properties of Nitrogen on Tungsten Films", by R. C. L. Bosworth, D.Sc., F.Inst.P.

"On Glacial Lakes in Kosciusko Region", by J. A. Dulhunty, B.Sc.

"The Eigen-Value Problem of Hill's Equation", by H. Schwerdtfeger, D.Sc.

"Nomograms for some Astronomical Computations", by H. W. Wood, M.Sc., A.Inst.P., F.R.A.S.

"Some Difficulties in Lewis and Calvin's Theory of Light Absorption", by D. P. Craig, M.Sc.

"A Note on the Platinum Derivative of a Substituted Pyrromethene", by D. P. Mellor, D.Sc., and J. B. Willis, M.Sc.

"The Calculation of the Ground Movement for the Initial Impulses of Galitzin Seismographs", by D. J. K. O'Connell, S.J., M.Sc., D.Ph.

December 5th, 1945.

The six hundred and twenty-ninth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Thirty-nine members and three visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Leslie Vickery Waterhouse, a member since 1924.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Albert Shulman, Leslie Lionel Hall and Lewis Michael Simmons.

Lecture by Dr. W. G. Martin.—It was announced that members were invited to be present at a lecture to be given by the Reverend W. G. Martin, D.D., on Tuesday, December 11th, 1945, at 8 p.m., in the Botany Lecture Theatre, University of Sydney, the subject of the lecture being "To the Top of the world" (Canada's Farthest North).

Library.—The following donations were received: 64 parts of periodicals, two whole volumes and eight back numbers.

The following paper was read:

"Evaporation of Oxygen from a Tungsten Surface", by R. C. L. Bosworth, D.Sc., F.Inst.P.

Commemoration of Great Scientists.—The meeting was devoted to the commemoration of great scientists, the following addresses being given:

"Alessandro Volta", by Dr. David Myers.

"William Roentgen", by Professor O. U. Vonwiller.

"Institution of the Alfred Nobel Prize", by Dr. D. P. Mellor.

Exhibits.—The following exhibits were arranged:

"X-ray Tubes", by B. W. Scott, B.Sc.

"Light Figures used in the Orientation of Quartz Sections", by Miss F. M. Quodling, B.Sc.

G. D. OSBORNE, President.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : The late T. Hodge-Smith (until June 8th), Mr. H. O. Fletcher.

Honorary Secretary : Mr. J. A. Dulhunty.

Five meetings were held during the year, the average attendance being twelve members and four visitors.

Meetings.

April 20th.—Notes and Exhibits : By Dr. Walkom : *Glossopteris* leaves attached to the stem in close spirals at the top of the branch, from Upper Coal Measures, Wallerawang. By Dr. Browne : Sandstone from Warragamba showing silification and the presence of kaolinite. By Mr. Lambeth : Lepidolite in felspar from Londonderry, Western Australia. By Miss Quodling : Nörrenberg method for orienting quartz, now used commercially. By Mr. Hodge-Smith : Specimen of King Island scheelite in garnet hornfels and scheelite crystals from Nundle. By Mr. Dulhunty : Lignite from New Chum Hill showing physical changes accompanying dehydration. By Mr. Whitworth : Notes on the production of zircon and rutile on the beaches of northern N.S.W. and Queensland.

June 15th.—Address by Prof. E. S. Hills, " Some Aspects of the Geology of Victoria in Light of Recent Research ".

July 20th.—Notes and Exhibits : By W. R. Browne : Possible correlation of Pre-Cambrian of North America and Australia. By Mr. Kenny : Grooved limestone from Mount Gambier, South Australia. By Dr. Walkom : *Osmundites* (Jurassic) from the Tibooburra district. By Mr. Lambeth : Phase diagram for felspars and kaolin. By Miss Quodling : Photograph of etched basal plane of quartz covered with plastic (polyvinyl acetate in ethylene dichloride). By Mrs. Sherrard : (*a*) Asbestos from Clarence district ; (*b*) Basalt which may have been the source of heavy mineral concentrates on the North Coast. By Mr. Fletcher : (*a*) Ammonites from Tibooburra showing iridescent lustre ; (*b*) *Linoproductus springsurensis* from the Hunter Valley. By Mr. Dulhunty : Brown coal from Victoria containing small quartz crystals and note on occurrence at Yallourn.

September 21st.—Discussion of Professor W. R. Browne's Presidential Address to the Linnean Society, " An Attempted Post-Tertiary Chronology for Australia ".

November 16th.—Address by Dr. G. D. Osborne, " Researches in the Hunter-Manning Region ".

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AUSTRALASIAN MEDICAL PUBLISHING COMPANY LIMITED

JOURNAL AND PROCEEDINGS

OF THE

ROYAL SOCIETY

OF NEW SOUTH WALES

FOR

1946

(INCORPORATED 1881)

VOLUME LXXX

Parts I-IV

EDITED BY

D. P. MELLOR, D.Sc.

Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

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GLOUCESTER AND ESSEX STREETS

Issued as a complete volume, September 9, 1947

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Part I *

Part II †

Part III ‡

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* Published January 13, 1947.

† Published May 1, 1947.

‡ Published July 23, 1947.

Part IV *

* Published September 9, 1947.

NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the " Philosophical Society of Australasia " ; after an interval of inactivity, it was resuscitated in 1850, under the name of the " Australian Philosophical Society ", by which title it was known until 1856, when the name was changed to the " Philosophical Society of New South Wales " ; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the " Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

The following publications of the Society, if in print, can be obtained at the Society's **Rooms**, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862–5, pp. 374, out of print.

Vols.	I–XI	Transactions of the Royal Society, N.S.W.,					1867–1877		,,	
Vol.	XII	Journal	and	Proceedings	,,	,,	1878,	pp.	324,	price 10s. 6d.
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Royal Society of New South Wales

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H. O. FLETCHER.
F. N. HANLON, B.Sc.
P. HINDMARSH, M.A., B.Sc.Agr.
R. S. NYHOLM, M.Sc.
D. J. K. O'CONNELL, S.J., M.Sc., F.R.A.S.
J. L. STILL, B.Sc., Ph.D.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

as at March 1, 1947

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney.
1938	P 2	‡Albert, Adrien, Ph.D. *Lond.*, B.Sc. *Syd.*, A.R.I.C. *Gt. B.*, Commonwealth Research Fellow in Organic Chemistry, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
1935		‡Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		‡Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		‡Alldis, Victor le Roy, L.S., Registered Surveyor, Box 57, Orange, N.S.W.
1909	P 12	‡Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.E. *Syd.*, M.Sc., Ph.D. *Cantab.*, A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 2	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1946		Barclay, Gordon Alfred, 168 Victoria-road, Bellevue Hill.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1946	P 4	Beattie, Joan Marian (Mrs.), B.Sc., Box 92, P.O., Cobar.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (*Oxon.*), 6 Beechcroft-road, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1946		Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carabella-street, Kirribilli.
1933	P 28	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., International Wool Secretariat, Grand Building, Trafalgar Square, London, W.C.2. (President, 1935.)
1939	P 11	Bosworth, Richard Charles Leslie, D.Sc. *Adel.*, Ph.D. *Camb.*, F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont; p.r. 41 Spencer-road, Killara.
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 19 Handley-avenue, Thornleigh.
1946		Breyer, Bruno, M.D., Ph.D., M.A., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney.

Elected.		
1940		Brigden, Alan Charles, B.Sc., 8 Clifford-avenue, Manly.
1919	P 1	Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
1942		Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
1935	P 4	Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. *Aust.*, 87 Ashley-street, Chatswood.
1913	P 22	Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
1940		Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
1946		Bullen, Keith Edward, M.A., B.Sc. (*N.Z.*), M.A. (*Melb.*), Ph.D., Sc.D. (*Camb.*), Professor of Applied Mathematics, University of Sydney, Sydney.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1940	P 1	Cane, Reginald Frank, D.Sc., A.A.C.I., General Motors-Holdens Ltd., Fishermen's Bend, Melbourne, Victoria; p.r. 2 David-street, St. Kilda, S.2.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 2	Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania.
1903	P 5	‡Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
1945		Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster Laboratory; p.r. Flat 4, 13 Milson-road, Cremorne.
1944		Cavill, George William Kenneth, M.Sc., Department of Chemistry, Technical College, Harris-street, Ultimo; p.r. 40 Chandos-street, Ashfield.
1913	P 4	Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
1940		Chambers, Maxwell Clark, B.Sc., 58 Spencer-road, Killara.
1913	P 21	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.Sc., A.I.F., 80 "St. James," Stanley-street, Sydney.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 34 Euroka-street, Northbridge.
1940	P 2	Colditz, Margaret Joyce, M.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 7 Wolsten-avenue, Turramurra.
1940	P 1	Cole, Joyce Marie, B.Sc., 7 Wolsten-avenue, Turramurra.
1940		Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
1946		Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1945		Coombes, Arthur Roylance, A.S.T.C. (Chem.), 14 Georges River-road, Croydon.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1937	P 8	Cornforth, Rita Harriet, D.Phil. (*Oxon.*), M.Sc. (*Syd.*), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
1940		Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
1909	P 7	‡Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1941	P 1	Craig, David Parker, c/o Chemistry Department, University College, London.
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street., Rockdale.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		‡Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.

Elected.		
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1946		Donohoo, Norma Winifred, B.Sc., 41 Second-street, Ashbury.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 9	Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney; p.r. 40 Manning-road, Double Bay.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 34	Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
1945		Eade, Ronald Arthur, B.Sc., 13 Steward-street, Leichhardt.
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.R.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
1937		English, James Roland, L.S., Water Conservation and Irrigation Commission, Sydney.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1944		Erhart, John Charles, Chemical Engineer, 33 Beaconsfield-parade, Lindfield.
1908		‡Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. *Lond.*, A.R.A.I.A., 6 Major-street, Coogee.
1944		Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
1939		Faull, Norman Augustus, B.Sc., A.Inst.P., c.o. National Standards Laboratory, University Grounds, City-road, Chippendale.
1909	P 7	‡Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
1940		Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1933		Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		‡Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 6 "Trinity Court," Telopea-street, Wollstonecraft.
1940		Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1944	P 1	Friend, James Alan, 16 Kelburn-road, Roseville.
1945		Furst, Hellmut Friedrich, B.D.S. (*Syd.*), D.M.D. (*Hamburg*), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.
1935	P 2	Garretty, Michael Duhan, M.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1942	P 3	Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1940		Gillis, Richard Galvin, 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1935		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney
1936		Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill.
1940		Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.

Elected.		
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture ; p.r. 151 Wollongong-road, Arncliffe.
1946		Gutmann, Felix, Ph.D., Commonwealth Research Fellow, Faculty of Agriculture University of Sydney, Sydney.
1945		Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney ; p.r. 15A Wharf-road, Longueville.
1892		‡Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney ; p.r. 23 March-street, Bellevue Hill.
1940	P 4	Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney.
1905	P 6	‡Harker, George, D.Sc., F.A.C.I. ; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1946		Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney.
1929		Hawley, J. William, J.P., Financial Agent.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord ; p.r. 34 Nicholson-street, Chatswood.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945		Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd. ; p.r. 10 Cremorne-road, Cremorne.
1938	P 4	Hill, Dorothy, M.Sc. *Q'ld.*, Ph.D. *Cantab.*, Geological Research Fellow University of Queensland, Brisbane.
1946		Hinder, Nora (Miss), B.Sc. (*Syd.*), 45 Clanville-road, Roseville.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director British General Electric Co. Ltd. ; p.r. " Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), " St. Cloud," Beaconsfield-road, Chatswood.
1916		Hoggan, Henry James, A.M.I.M.E. *Lond.*, A.M.I.E. *Aust.*, Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 6	Hughes, Gordon Kingsley, B.Sc., Senior Lecturer in Chemistry, University of Sydney, Sydney.
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney ; p.r. " Belbooree," 10 Wandella-avenue, Roseville.
1943		Iredale, Thomas, D.Sc., F.R.I.C., Reader in Chemistry, Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1940		Johns, Thomas Harley, 130 Smith-street, Summer Hill.
1946		Johnson, Guy Frederick, 644 Botany-road, Alexandria.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney ; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935		Kelly, Caroline Tennant (Mrs.), " Eight Bells," Castle Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney ; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1943		Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo ; p.r. 18 Lyne-road, Cheltenham.

Elected.		
1945		Laing, Norma Dorothy, B.Sc., Biochemist, 58, Hopetoun-avenue, Vaucluse.
1939	P 1	Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., P.O. Box 21, Concord.
1946		Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1936	P 2	Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 55	‡Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader in Chemistry, Department of Chemistry, University of Sydney.
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 3	Lipson, Menzie, B.Sc., A.A.C.I., Chemist, c/o Department of Textile Industry, Leeds University, Leeds 2, England.
1940	P 1	Lockwood, William Hutton, B.Sc., Food and Agricultural Division, Zonal Executive Offices, Control Commission for Germany, Shell Haus, Hamburg, B.A.O.R., Germany.
1906		‡Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1943		Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 8 Boronia-avenue, Wollstonecraft.
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943		McCoy, William Kevin, Analytical Chemist, R.A.A.F.; p.r. 16 Bishop's-avenue, Randwick.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	‡McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	‡McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 3	McKenzie, Hugh Albert, B.Sc., Assistant Research Officer, C.S.I.R.; p.r. 52 Bolton-street, Guildford.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Technological Museum, Harris-street, Ultimo; p.r. 14 Orwell-street, Potts Point.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1943		McNamara, Barbara Joyce (Mrs.), M.B., B.S., Dimbulah, North Queensland.
1946		McPherson, John Charters, "Greenleys," No. 6 Wallaringa-avenue, Neutral Bay.
1946		McRoberts, Helen May, B.Sc., 16 Grosvenor-road, Lindfield.
1940		Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1946		May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
1935	P 1	Maze, Wilson Harold, M.Sc., Lecturer in Geography, University of Sydney.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 23	Mellor, David P., D.Sc., F.A.C.I., Reader in Chemistry Department, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42 Joint Hon. Secretary.)
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1940		Mercer, Edgar Howard, Textile Department, University of Leeds, Leeds, England.
1928		Michell, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1943		Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street, Rockdale.
1945		Morris, Samuel, A.S.T.C. (Chem.), A.A.C.I., F.C.S.G.B., 217 Burns Bay-road, Lane Cove.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 27	Morrison, Frank Richard, A.A.C.I., F.C.S., Economic Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo. (Joint Hon. Sec.)
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.

Elected.		
1944		Moye, Daniel George, Chemist, Warragamba Dam.
1946		Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
1915		Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., F.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Government House, Port Moresby, Papua.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld.
1943		Neuhaus, John William George, c/o Meggitt Ltd., Parramatta.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Botany, Victoria University College, P.O. Box 1580, Wellington, N.Z.
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets, Coogee.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1945		Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Secretary, Linnean Society of N.S.W., Science House, Gloucester-street, Sydney.
1920	P 4	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 21	Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
1935	P 4	O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1921	P 6	Osborne, George Davenport, D.Sc. *Syd.*, Ph.D. *Camb.*, Lecturer and Demonstrator in Geology in the University of Sydney. (President, 1944.) (Hon. Treasurer.)
1920	P 74	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.)
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliff.
1946		Pinwell, Norman, B.A. (*Q'land*), The Scots College, Bellevue Hill.
1943		Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		‡Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1946		Potter, Bryce Harrison, B.Sc. (Hons.) (*Syd.*), 13 Fuller's-road, Chatswood.
1921	P 2	Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1945		Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1945		Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
1893		‡Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 6	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940	P 2	Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.

Elected.		
1919	P 3	Rancland, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Mineral Resources Survey, Department of Supply and Shipping, Census Building, Canberra, A.C.T.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1946		Rhodes-Smith, Cecil, 261 George-street, Sydney.
1939	P 15	Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney.
1939	P 3	Robbins, Elizabeth Marie (Mrs.), M.Sc., 36 Cambridge-street, Epping.
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1945		Rountree, Phyllis Margaret, M.Sc. *Melb.*, Dip.Bact. *Lond.*, 25 Elizabeth Bay-road, Elizabeth Bay.
1945		Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory; p.r. 83 Woniora-road, Hurstville.
1945		Sampson, Aileen (Mrs.), Sc.Dip. (A.S.T.C., 1944), 54 Young-street, Croydon.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 2	Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1946		Scott, Beryl (Miss), 3 Lanyon Flats, 46 Upper Bayview-street, North Sydney.
1940		Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, 2 Edward-street, Gordon.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
1945		Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1945	P 2	Simmons, Lewis Michael, B.Sc. (Hons.) *Lond.*, A.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1900		Simpson, R. C., 24 Earl-street, Roseville.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, New College, Oxford, England.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	‡Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney; p.r. 79 Ocean-street, Woollahra.
1940		Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.

Elected		
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. *Adel.*, c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Flight-Lieutenant, R.A.A.F., M.Sc., A.Inst.P., 17 Millicent-avenue, Toorak, Melbourne, E.2, Victoria.
1946		Thomas, Ifor Morris, M.Sc., St. Andrew's College, Newtown.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.
1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.)
1943		Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1945		Walters, Laurence Gordon, B.Sc., Flat 3, 33 Gould-street, Bondi.
1913	P 5	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S. F.R.Z.S., c.o. Australian Museum, College-street, Sydney.
1919	P 1	Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 6	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor in Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1944		Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
1945		Webster, Evelyn May, B.Sc., Chemist, 2 Buena Vista-avenue, Mosman.
1920		Wellish, Edward Montague, M.A., Emeritus Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1946		Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.

Elected.		
1940	P 1	White, Douglas Elwood, M.Sc., D.Phil., University of Western Australia, Nedlands, W.A.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., c.o. Davis Gelatine (Aust.) Pty. Ltd., Spring-street, Botany.
1944	P 1	Willis, John Bryan, B.Sc., Chemistry Department, University College, London.
1945		Willis, Jack Lehane, B.Sc., Flat 5, "Narooma", Hampden-street, North Sydney.
1943		Winch, Leonard, B.Sc., Chief Chemist, Fielder's General Products Ltd., P.O. Box 143, Tamworth, N.S.W.
1940		Wogan, Samuel James, Range-road, Sarina, North Queensland.
1936	P 4	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer, Sydney Observatory, Sydney.
1906	P 12	‡Woolnough, Walter George, D.Sc., F.G.S., 9 Lockerbie Court, East St. Kilda, Victoria. (President, 1926.)
1945		Wright, Barbara, B.Sc., Biochemist, "Derribong," Ada-avenue, Wahroonga.
1916		Wright, George, Company Director, c.o. Hector Allen, Son & Morrison, A.M.P. Chambers, 89 Pitt-street, Sydney.
1946		Wyndham, Norman Richard, M.D., M.S. (*Syd.*), F.R.C.S. (*Eng.*), F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.

Honorary Members.

Limited to Twenty.

1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1946	Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E. 10, England.
1946	Jones, F. Wood, D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (*Lond.*), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England.
1915	Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.

Obituary, 1946-1947.

1921 Henry Gordon Farnsworth.
1911 Sir George A. Julius.
1901 Carl Adolph Sussmilch.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.

"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.

"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.

"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (This Journ., 1936, *70*, 39.)

1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (This Journ., 1937, *71*, 68.)

1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E. D.Sc. (Oxon.). (This Journ., 1938, *71*, 503.)

1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (This Journ., 1939, *73*, 41.)

1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (This Journ., 1940, *74*, 283.)

1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (This Journ., 1941, *75*, 47.)

1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.

1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.

1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.

1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.

1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 *to* 1878.

The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.

Awarded.

1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.Sc., F.G.S.
1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
1909 *Dr. Walter E. Roth, B.A.
1912 *W. H. Twelvetrees, F.G.S.
1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.Sc.
1922 *Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.
1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."

1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.

1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.

1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.

1940 G. J. Burrows, B.Sc., University of Sydney.

1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.

1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.

1946 Briggs, L. H., D.Phil. (*Oxon.*), D.Sc. (*N.Z.*), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.

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EDITED BY
D. P. MELLOR, D.Sc.
Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

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CONTENTS

VOLUME LXXX

Part I

PRESIDENTIAL ADDRESS

By Adolph Bolliger, Ph.D.

Delivered to the Royal Society of New South Wales, April 3, 1946.

Part I. THE PAST YEAR.

The war in Europe terminated at the beginning of the financial year, and the war in the Pacific came to a sudden end a few months later. During this eventful period and its turbulent aftermath, our Society functioned in the usual manner, and not even the atomic bomb was able to upset its equilibrium. One might have expected a sudden increase of activity, large numbers of members attending the meetings and more papers presented. This, however, has not yet come to pass, but it is with the greatest anticipation that we look towards the coming year.

Nevertheless, a satisfactory standard has been maintained: the number of members has increased to 300, and 22 papers have been presented for reading and publication. In addition, four lecturettes were given by the following speakers: Miss P. M. Rountree, Messrs. J. B. D. Penninck, N. A. Whiffen and H. W. Wood. Exhibits were presented by Miss F. M. Quodling, Dr. D. P. Mellor and Mr. B. W. Scott.

Symposia on "Fluorine" (Drs. N. E. Goldsworthy, F. Lions and D. P. Mellor) and "Visual Education" (Squadron Leader N. Rosenthal and Mr. J. C. Storey) were well attended and greatly appreciated.

At the December general monthly meeting lectures by Dr. David Myers on "Alessandro Volta", Professor O. U. Vonwiller on "Wilhelm Roentgen", and Dr. D. P. Mellor on "The Institution of the Alfred Nobel Prize" commemorated the achievements of these great scientists.

Due to the sudden cessation of hostilities it has only been possible to hold four popular lectures. The lectures were:

June 21st.—"The Chemistry of Water and Washing", by R. S. Nyholm, M.Sc.

July 19th.—"Penicillin and its Medical Uses", by Jean Armytage, M.B., B.Sc., M.R.A.C.P.

September 20th.—"The Mediterranean—Past and Future", by Professor A. H. McDonald, M.Sc., Ph.D.

November 15th.—"Liquid Life", by Professor G. G. McDonald, B.Sc., Ph.D.

The Clarke Memorial Lecture for 1945 was delivered by Professor E. S. Hills, D.Sc., Ph.D., on June 13th, the title being "Some Aspects of the Tectonics of Australia", and the Clarke Memorial Medal for 1945 was awarded to Professor W. N. Benson of the University of Otago, Dunedin.

The Society owes an apology to its members for the fact that during the last few years, owing to war conditions and strikes, the completed Journal has always been late in appearing. The 1944 volume, which under normal circumstances should have been in the hands of members early in 1945, will be received in May, 1946. However, efforts are being made to remedy the situation and the 1945 volume will become available to members in the second half of 1946. After

this it is anticipated that subsequent volumes will be on time. In future authors of papers will receive reprints within a month or two of their submission to the Council. Simultaneously, efforts are being made to increase the circulation of our Journal by sending it to a large number of scientific institutions which previously did not have it in their libraries.

The future of our Society may be greatly influenced by the fact that it has been decided to enlarge Science House. Science requires proper quarters in order to function, a thought which found its expression in the present building in Gloucester Street, of which the Royal Society is part-owner. It is, however, inadequate for present-day requirements, and definite plans have been made for its enlargement into York Street. Though the erection of the additional building is out of the question at present, the Society most gratefully acknowledges to the Government of New South Wales the gift of the land on which the addition will be built. It is planned to have, in addition to the present accommodation, a large, up-to-date lecture room, a central library and a comfortable reading room.

It is with regret that I have to announce that the Society lost by death eight of its members, amongst them our Honorary Treasurer, Mr. Allan Clunies Ross. He will long be remembered for his untiring efforts for the benefit of the Society.

As usual the great burden of work connected with the smooth running of our Society was borne by the Honorary Secretaries, Professor Elkin and Dr. Mellor, and the Society is greatly indebted to them. Our thanks are also due to the Honorary Librarian, Mr. H. W. Wood, for his keen interest in library affairs.

At this point I would like to mention that Professor Elkin, who has held the office of senior Honorary Secretary for the last ten years, is about to retire. His services to the Society have been many and of the highest order. Through his unceasing efforts the Society has been kept running efficiently through difficult years and his retirement will be a serious loss to the Society.

Part II. SOME ASPECTS OF MARSUPIAL REPRODUCTION.

Introduction.

Scientists arriving recently from abroad have indicated that the flora and particularly the fauna of this country are still Australia's greatest advertisement. I therefore believe that it is almost a duty of suitably placed Australian scientists to make full use of this great and far from fully explored asset. Undoubtedly, the main attraction in the Australian animal kingdom are the primitive mammals, the monotremes and the marsupials, and in these probably the greatest interest centres around the mode of reproduction.

At the Gordon Craig Laboratory, University of Sydney, over the last nine years monotremes and marsupials were studied. Particular attention was paid to the easily procurable Australian opossum or phalanger, *Trichosurus vulpecula*, commonly called possum, which in contrast to the polyprotodont American opossum (*Didelphys virginiana*) is a diprotodont, a group of marsupials exclusive to Australia and the islands to the north of it, and a number of observations were made which have a bearing on the problem of reproduction of marsupials. It was considered that the present occasion was an auspicious one to present some of these observations within the framework of a short thesis on this problem which as yet is only partially understood.

Some Historical Notes.

Referring to marsupials the great John Hunter in 1780 wrote in his essay of the opossum from New Holland that " there is something in the mode of

propagation in this animal that deviates from all others". He also said, however, that he did not possess "sufficient information to complete our knowledge of the system of propagation in this class" and, unfortunately, he was unable to study the problem further before his death which took place in 1793. More than a century after Hunter made this remark, J. P. Hill (1899), working on the bandicoot at the University of Sydney, gave us the first definite information of the mechanism of marsupial birth.

However, the morphology of the internal organs of reproduction in the female marsupial had attracted the attention of the earliest observers and already, almost a hundred years before Hunter and practically two hundred and fifty years from today, Tyson (1698) gave the first description of the female internal organs of reproduction of the American opossum, *Didelphys virginiana*. Sir E. Holme (1785), the son-in-law of John Hunter, apparently was the first to give a description of the female reproductive organs of a typically Australian marsupial, the kangaroo.

The pioneer observations of Tyson (1698) and Holme (1785) were incorrect in important points; for example, they mistook the vagina for the uterus. In the nineteenth century the true relationship of the different organs of reproduction was slowly established and writers such as Cuvier and Blainville in France, Barton and Owen in England, Brass and von Stirling in Germany and Hill in Australia, to mention only a few, dealt with the anatomy of the genital tract of marsupials. Van den Brock (1905) in Holland summarized the findings of the previous workers and added many new observations to the morphology of these organs and he later on also dealt with the male reproductive tract (1910). In many respects van den Brock's work represents the coping stone in the elucidation of the morphology of the marsupialian genital organs, a problem which had occupied the brilliant minds as well as the lesser lights of many lands.

General Anatomy of the Female Internal Reproductive Organs of Marsupials with Special Reference to Trichosurus vulpecula.

In comparing the anatomy of the organs of reproduction of female marsupials with those of other mammals, one is struck by a rather more complicated arrangement. They consist of two ovaries, two tubes, two uteri, three vaginæ (a median and two lateral ones) and the uro-genital sinus. (Plate I, Figs. 1, 2.)

From each ovary the oviduct or tube proceeds medially and enters a uterus. The two uteri are inserted into the median vagina. The lower end of the median vagina is attached to but does not communicate with the uro-genital sinus. A few millimetres lateral to the points where the uterine cervices enter the median vagina, the lateral vaginæ are inserted. The lateral vaginæ are two tube-like structures, one on either side of the mid-line extending between the median vagina and the uro-genital sinus. The ureters pass down the posterior wall of the pelvis and on reaching the pelvic floor curve around in a sling-like fashion between the lateral and median vaginæ to enter the bladder in a cephalad direction. The median vagina of *Trichosurus vulpecula* contains a median septum which is ruptured with the first pregnancy.

According to van den Broek, a fundamental difference between marsupials and mammals in general lies in the fact that in the case of the marsupials the ureters pass in between the oviducts and thus prevent the oviducts from meeting in the mid-line to form a single median uterus and vagina. Wood Jones (1943) actually defined a marsupial as a mammal whose kidney ducts lie mesial to the oviducts. In higher mammals the ureters run lateral to the oviducts and the oviducts therefore are in no way obstructed from combining in the mid-line to form a median uterus and vagina.

AA—April 3, 1946.

Notes on Development.

Nature apparently first intended the marsupials to be oviparous, as is the case with the monotremes (platypus and echidna). The original design was simple, namely a tube extending between each ovary and the uro-genital sinus. As development advanced, this tube became subdivided into four components. The upper end retained its original function, namely the transport of the ovum. The next portion became thickened to form a uterus, while the third sections of both tubes united in the mid-line to form a single median vagina. In the process of fusion a septum is formed which in the case of *Trichosurus vulpecula* persists in the mid-line of the median vagina until the first pregnancy, when it breaks down. In the fully grown parous possum the median vagina has roughly the shape of an inverted triangle of about 3 cm. in height. The width of the base of the triangle, which is perforated by the uterine cervices, is about 2·5 cm. The apex of the triangle is attached to the uro-genital sinus and is separated from its lumen by a substantial layer of tissue.

The fourth and lowest portion of the tube developed into the lateral vagina, which in *Trichosurus vulpecula* is about 2·5 cm. in length and 0·25 cm. in width.

The formation of the median vagina has been explained by the fact that the ureters pass in between the oviducts and enter the bladder in a sling-like fashion in a cephalad direction. A section of the original oviduct below the level of the uterus sagged inwards towards the mid-line over the slings formed by the ureters. In the female embryo of *Trichosurus vulpecula*, for example, the two sagging tubes can be seen to develop (Buchanan and Fraser, 1918), still independent from each other. In the pouch young the two blind passages referred to as culs-de-sac meet in the mid-line and their adjacent walls fuse to form a structure known as median vagina.

Reproductive Process.

In the process of reproduction the egg shed from the ovary is fertilized high up in the oviduct, and as a fertilized ovum it moves towards the exterior. In one of the two uteri, however, it is embedded and vascular connection with the tissues of the mother for the purpose of obtaining nourishment is created. Thus within a very short period of about two weeks is formed an embryo of considerable size which is now seemingly too large to move to the exterior through one of the lateral vaginæ. As a result the fœtus moves into the larger median vagina and is temporarily without an obvious outlet. Now a rupture of tissue which produces a birth canal occurs at the spot where the lower end of the median vagina is attached to the upper part of the uro-genital sinus and the fœtus is now born through the uro-genital sinus after a period of gestation of approximately sixteen to eighteen days. The newly born young being unable to lead a life separate from its mother on account of its immature state, corresponding roughly to a four to five months human fœtus, moves into the pouch and attaches itself to one of the two nipples and remains there for at least another four months till it becomes capable of living outside the marsupium of its mother.

The Pouch, an External Organ of Reproduction.

(*a*) *Historical Notes.* The external pouch or marsupium which is present in most still existing marsupials in various degrees of development had and still has a marked influence on the imagination of lay minds who gave it prominence in their writings and arts. This was already so in prehistoric times. In central America, in a grave of pre-Columbian days, a golden bell was found fashioned in the image of the female opossum, the pouch being exaggerated and expanded and containing pebbles. Shortly after the discovery of America, fantastic accounts of the function of the pouch of marsupials then met with for

the first time by the white man were published and are referred to by Tyson (1698). They were mostly based on the idea that the pouch was really the uterus of the animal and that the young developed in there after the fertilized egg had somehow been deposited into the pouch or that the fœtus was born through the mammary glands into it, or that the young were blown into the pouch from the nostrils of the females. Similar ideas were also commonly expressed in Australia and are still believed by certain people.

(*b*) *Theories on Developmental Anatomy.* The modern scientific literature on the pouch of marsupials is comparatively small. From a morphological point of view not much could be said about this cavity on the abdomen of the female which usually was considered to be secondary to the development of the mammary glands contained by it. Developmentally it was explained by Klaatsch (1891) and confirmed by Breslau (1920) to have originated from the so-called marsupial pockets which are circular indentations found around the mammæ of young animals. Enders (1937) traces the development of the pouch from the epidermal ridge found to be present on the abdomen of the newly born though sexually undifferentiated young and considers the formation of the pouch due to the expansion of the mammary area. In short, according to Enders, the pouch is formed when the ridges which constitute the lips of the pouch in later life remain stationary and the expanding mammary area throws the skin into a double-walled fold. Somehow none of these explanations seemed to be very satisfactory and a certain tendency became evident to ignore the pouch as a characteristic of higher developed marsupials. Thus Abbie (1941) writes: "To the contention that pouch formation is decidedly distinctive may be opposed the fact that the muscular apparatus upon which it depends is the same as that of any other primitive mammal, and the insunken mammagenous skin comes from the same region; only the hiatus which permits its formation is really peculiar."

However, recent work on *Trichosurus vulpecula*, which possesses a very marked pouch, which has in part already been presented before this Society (Bolliger, 1942*a*), has suggested that the pouch is homologous to the male scrotum and may be considered an inverted scrotum.

The Male Reproductive Organs and Their Function.

The female of the order marsupialia, with its pouch and its three vaginæ, undoubtedly received most of the scientific limelight and the male was only a marsupial because of his mate. It seemed to be tacitly assumed that he possessed nothing nearly as interesting as, for example, the temporary birth canal. However, work done within the last few years at the Gordon Craig Laboratory brought out the fact that the male of *Trichosurus vulpecula*, as well as of other marsupials, show sexual peculiarities of great interest.

In the first place it was noticed that the sexually mature male of *Trichosurus vulpecula* throughout his life produces spermatozoa which appear constantly in the urine (Bolliger and Carrodus, 1938; Bolliger, 1942*a*). Many of these spermatozoa when voided show signs of life, and occasionally some or many are strongly motile. This persistent physiological spermatorrhœa is unusual in mammals where spermatozoa are ejaculated in definite short periods and are usually separated from urine. If eutherian spermatozoa come into contact with urine they cease to be motile and die.

The accessory genital organs of *Trichosurus vulpecula* and of other marsupials are also remarkable if compared with those in the mammalia in general. The large testes and epididymes which are prepenile are connected with a thin vas deferens poorly endowed with muscle and possessing no ampulla and leading directly into the prostatic urethra. No seminal vesicles are present whose secretions add dilution and lubrication to the spermatozoa. In our marsupial

the masses of spermatozoa pile up in the wide urethra to be flushed out with the urine on micturition.

The prostate itself, a carrot-shaped organ surrounding the urethra, is of very large dimensions. In *Trichosurus vulpecula* it is the largest organ in the abdominal cavity excepting the liver. Its acini secrete a viscous fluid into the remarkably wide prostatic urethra traversing its long axis. This viscous prostatic secretion frequently gives to the urine a markedly oily appearance and again it seems as if the prostatic secretion was an almost permanent one, though with some variations in quantity. This constant secretion of spermatozoa and prostatic secretion in the urine brings up the question as to what are the conditions to be fulfilled for a fertile copulation. Is it necessary for the animal to exclude urine as much as possible and to obtain a mixture consisting almost solely of spermatozoa and prostatic secretion. This is probably doubtful in view of the fact that spermatozoa may be motile even in a large volume of urine, but in all probability a certain minimal concentration of prostatic secretion is required to ensure that the spermatozoa will be capable of fertilizing the ovum. However, further experimental work will be required to definitely solve this question.

In non-mammals such as reptiles and amphibia, the testes discharge spermatozoa to a part of the kidney, and consequently spermatozoa are transported through the kidney ducts to the exterior and are probably mixed with some urine. The spermatorrhœa of marsupials has been considered a remnant of this arrangement in reptiles and amphibia (Bolliger, 1942*b*). However, in these lower vertebrates the creation, as well as the subsequent transport, of spermatozoa is a seasonal affair and a definite process of ejaculation can be noticed. It may also be added that these animals usually possess comparatively large seminal vesicles. In the possum no marked seasonal influences were observed and practically every twenty-four hours in a sexually mature male some 1,000,000 to 10,000,000 spermatozoa slightly larger in size than those from human beings pass through the thin walled narrow vasa deferentia directly into the wide prostatic urethra. Therefore it seems that the male is capable of fertile copulation at any time, but probably is aroused to activity only when the female is " in heat ".

From a study of the anatomy of *Trichosurus vulpecula* it seems that in the absence of seminal vesicles the wide urethra as well as the surrounding mass of prostatic tissue are of prime importance to marsupialian reproduction. This was also indicated by the result of castration performed in adolescent males. The removal of the testes is followed by a practically complete abolition of the prostate gland as well as of the wide urethra typical of the male marsupial. What actually remained of the original prostate some months after castration was a slightly tapering tube about a tenth of its maximum width as seen in untreated animals and which, in the absence of glandular tissue, consists mostly of fibrous tissue. The circular appearance of the urethra was entirely lost. It now consisted of a number of longitudinal folds converging towards the centre, the entire lumen of the urethra being less than a tenth of that ot the normal prostatic urethra. The urethra of the castrated possum resembles that of females of higher mammals, the males of which are endowed with a much thicker vas deferens, seminal vesicles and ampulla. It may also be mentioned that in spite of this greatly diminished diameter of the urethra of the castrated animal, no ill effects such as urinary obstruction were noticed at any time. On this evidence, therefore, it seems rational to attribute a major function in reproduction to the wide marsupialian urethra (Bolliger and Tow, 1946).

If one tries to picture the mode of transport of the spermatozoa from the prostatic urethra to the fallopian tubes of the female one has to consider that the prostate contains no muscular tissue of any size between the acini. The whole organ, however, is enclosed by a thin layer (about 0·2 mm.) of smooth muscle

which would be capable of compressing the acini which it encloses in such a manner as to express considerable amounts of prostatic secretion into the prostatic urethra. The spermatozoa now mixed with a comparatively large amount of prostatic secretion would be forced from the membranous urethra into the cavernous or penile urethra. The viscous mixture containing the spermatozoa, after leaving the urethra by the external urethral orifice (meatus) would undoubtedly follow the flagellum-like horny projection on the tip of the penis next to the meatus and, like a drop of oil running along a rod, would ultimately have to reach the interior of one of the lateral vaginæ, the only available passage to the tubes. Though the actual details of copulation cannot be seen, it has been observed in males that such secretions follow the path as described. The spermatozoa and the vehicle in which they are suspended thus reach the median vagina from which they have to find a way up through the uteri into the tubes. It seems almost unavoidable that a certain amount of urine is mixed with the spermatozoa and prostatic secretion, particularly since copulation is not short-lived but may last for hours, and it may be possible that the urinary inflow into the prostatic urethra provides the force that drives the spermatozoa into the lateral vagina and from there into the median vagina.

In view of these considerations it is doubtful whether an ejaculation of semen as observed in higher mammals and in lower vertebrates occurs in marsupials, and it may also be stated that attempts on a bandicoot (*Perameles nasatu*) to bring on ejaculation by electrical stimulation have failed so far. Therefore, incomplete as our knowledge is, the process of reproduction as found in the male of *Trichosurus vulpecula* is quite different from what we find in higher mammals. It is also different from the processes as seen in reptiles and amphibia and therefore one may be permitted also to speak of a definite marsupialian reproduction as present in the male of the order.

At present, purely as a speculation, it may also be suggested that the act of copulation may serve in forming a passage or the beginning of a passage from the median vagina into the uro-genital sinus. As pointed out before, such a passage is required in the process of parturition and it seems rather strange that the very small fœtus should be required to penetrate this formidable tissue barrier unaided.

Some Effects of Hormones on the Internal Reproductive System of Marsupials.

(*a*) *Introduction.* During the last decade a number of very interesting substances were either isolated from natural sources or were synthesized in the chemical laboratory. They were collectively referred to as sex hormones. These naturally occurring substances are secretions provided through the activity of the gonads whose active crystalline principle is a sterol compound. The female sex hormones are referred to as œstrogens or gynogens and the male ones as androgens. At present, to the group of œstrogens such as œstradiol and its esters must be added other compounds chemically not related to the sterols, such as stilbœstrol and hexœstrol, which have the same physiological action as the natural œstrogens. These sex hormones, œstrogens and androgens alike control in a wide measure the morphology and physiology of the accessory and secondary organs of reproduction, a fact well demonstrated in their ability to prevent or repair the atrophy of accessory sex organs brought on by castration. Since, in short, the reproductive system is their main field of action, they have become a most important tool for the investigation of reproductive processes in man and animal alike. They have also been applied to the study of the reproductive organs and processes of *Trichosurus vulpecula* here in Sydney and almost simultaneously in U.S.A. to the study of *Didelphys virginiana*, a polyprotodont marsupial (Burns, 1939; Moore, 1941). The American authors, however, in

their investigation dealt exclusively with newly born animals up to the age of about 100 days, while we used specimens which were at least two months old and which were observed for a number of months or even years. The response of fully grown animals was also studied.

(*b*) *Experimental Findings*.—(1) *Œstrogen Administration to Females*. Following the administration of œstrogens (œstrone, œstradiol, benzoate, œstradiodipropionate, stilbœstrol and hexœstrol) the most striking finding was the response of the median vagina (Carrodus, A., 1941). Three distinct stages were observed : (α) œstrus distension, (β) giant vagina, (γ) pyovagina.

(α) Œstrus Distension. Œstrus distension may be considered to be the natural sequence to œstrogen administration in physiological amounts because in the normal female œstrous is characterized firstly by hyperplasia of the epithelium of the vagina, which is followed by cornification and desquamation. Following this, fluid accumulates in the median and lateral vaginæ. Subsequently, leucocytic invasion occurs and the normal bacterial flora proliferates and becomes instrumental in the removal of desquamated epithelium and ketatinous débris. Some of the accumulated fluid escapes to the exterior and the rest is absorbed. Thus the vaginæ return to the resting stage, which is accompanied by epithelium regression and repair (Hartman, 1923).

(β) Giant Vagina. If, however, the administration of œstrogen is continued, more fluid accumulates and a greater distension is produced, resulting in a giant vagina full of aseptic pus, and with continued œstrogen administration one should expect a still greater distension.

(γ) Pyovagina. However, under these conditions of prolonged œstrogen administration or after the injection of a very large single dosage of œstrogen, secondary infection by pyogenic organisms from the lower genital tract soon occurs, filling the distended vagina with pus and bringing on the death of the animals from the absorption of the toxic products of the infection. Simultaneously also severe urinary obstruction occurs due to the pressure of the distended median vagina on the ureters (Plate II, Figs. 1, 2).

Comment. The creation of a giant vagina and subsequently pyovagina brings up the question how is it that the animal cannot relieve the distension in the median vagina by draining some of the fluid to the exterior ?

The lateral vaginæ would provide an outlet for the excess fluid, particularly since they are definitely enlarged in animals treated with œstrogen. But typical œstrogen reactions such as thickening of the epithelium and accumulation of débris, especially at the lower end, constitute a serious obstruction which, in the first place, is the cause of the distension of the median vagina. This tension could also be relieved and the life of the animal prolonged by forming an opening between the median vagina and the uro-genital canal, a process which occurs during birth. However, no communication of such a nature could be detected in any of the specimens treated with œstrogen. Not even squamous epithelial changes were demonstrated in the region of the tissue between the uro-genital sinus and median vagina. In some instances the distended median vagina emptied its contents into the abdominal cavity through a rupture through the anterior aspect of the organ. This indicates the degree of intravaginal tension. It also indicates that œstrogens are not connected with the formation of the temporary birth canal formed in *Trichosurus vulpecula* during birth and the question arises how is this tear, through a substantial tissue barrier, accomplished in the normal animal. Two possibilities may be considered as aiding the fœtus in this task. Firstly, during pregnancy a softening of the tissues by an unknown process at the lower end of the median vagina may predispose to the forcing of a passage into the uro-genital canal by the fœtus and secondly, a partial or complete passage was already established in the act of copulation some two weeks pre-

viously. However, no actual observations or experiments have as yet explained this phenomenon.

It was considered that the response of the genital tract of *Trichosurus vulpecula* to œstrogens enhanced the claim that median and lateral vaginæ belonged to the female (Mullerian) tracts as stated by embryologists.

It is of interest, however, to note that the drastic changes leading to the condition of pyovagina and death were produced by small doses of œstrogen, namely about 2 mgms. per kgm. body weight. Analogous changes have been produced in the uteri of rats and other rodents by a dosage at least ten times as great.

(2) *Testosterone Administration to Females.* Testosterone propionate, the male sex hormone used in this investigation, however, gave responses which in several respects were unexpected. After administering it to a half-grown animal over a period of five months (total amount administered, 230 gms.) it was noticed that a tense abdominal swelling began to appear in the suprapubic region, the animal showing no other ill effects at that time. This swelling increased rather rapidly and began to embarrass the animal which at this stage was killed. On post-mortem examination a most dramatic condition was encountered, i.e. a median vagina which was about twice as large as the head of the animal. It measured 9·3 cm. in width, 6·0 cm. in length and 6·0 cm. antero-posteriorly (Plate III, Fig. 1). The lateral vaginæ were visible as straight ridges running along the inferior aspect of the median vagina. The uteri were also considerably enlarged and the ureters were moderately dilated.

A hairless female pouch young treated with testosterone propionate for a shorter period of time (two months) with a total dosage of 55 mgms. of hormone developed prostatic tissue in the wall of the uro-genital canal. The vaginæ and uteri were also enlarged, but to a lesser extent than in the experiment mentioned previously.

Comment. These findings indicate that the male sex hormone had a strongly stimulating effect on the female reproductive organs of the possum. Similar findings were observed on American opossum *Didelphys virginiana*, which were treated with testosterone propionate immediately after they were born (Burns, 1939; Moore, 1941). The experiment executed here in Sydney brings out a number of points which may be emphasized. In the first place, the male hormone, testosterone propionate, acts on the female reproductive system as though it were a female sex hormone, with the one difference that testosterone is less toxic. It is apparently less abrupt in its action, giving the body more time to compensate for the changes brought on by the hormone. Consequently in our experiment the animal was able to survive the impact on the genital tract and to produce a median vagina of a size never obtained in experiments with œstrogen. No typical pyovagina formed, and in consequence a severe general reaction from the absorption of toxin was not noticed. Also, the nitrogen retention which always was most marked in œstrogen treated animals was practically absent. The other point which so far has only been noticed in our *Trichosurus vulpecula* is that this marked reaction occurred in an animal which was in the stage of advanced adolescence as the experiment was started and became of mature age during the progress of it. In other mammals similar experiments succeeded only in embryos or in very young specimens to anywhere near the same degree. This is of some importance not only from the developmental point of view but also because it is frequently of advantage to have at one's disposal a responsive animal at that critical period which is referred to as puberty and which is able to withstand the hazards of the experiments. Very young animals or embryos usually have a high mortality rate in experiments as described. This also applied to the experiments of Burns (1939) and Moore (1941) on the pouch young of *Didelphys virginiana*.

Summarizing the effects of œstrogens and testosterone on the internal organs of reproduction in the female of *Trichosurus vulpecula*, it may be said that the marsupial anatomy of these organs creates responses which, at least are different in a quantitative sense from those obtained from higher mammals, even if from theoretical or other considerations one should not be prepared to admit qualitative differences. Compounds of the nature of œstrogens or androgens do not seem to play an important roll in the birth process of marsupials.

Reactions of the Pouch to Sex Hormones.

It has been recorded in the proceedings of this Society that immediately after the administration of œstrogens the pouch of the fully grown *Trichosurus vulpecula* becomes swollen, as particularly evidenced by a thickening of the lips. Within a few days this swelling is followed by a severe contraction which may almost completely eliminate the marsupium. This contraction, however, is not permanent, and within a few weeks the pouch expands again to its original size (Bolliger and Carrodus, 1938). In the natural process of reproduction a somewhat similar contraction of the pouch is noted after the young has left the pouch and the mother prepares herself for the next breeding season.

Testosterone in young animals brings on a precocious development of the pouch which, however, also contains the typical elements of œstrogen action, namely, swelling and contraction. But in spite of sustained injections of the androgen, this is followed by a decrease in size which may almost amount to atrophy. This latter development prevails in fully grown animals and the early response as seen in the young is hardly perceptible.

If, however, the adolescent female is castrated before the administration of testosterone, the lips of the pouch thicken, but they also become everted in such a manner that no pouch recess exists and the two longitudinal pendulous ridges formed fully expose the small atrophic nipples as shown in Fig. 1 (3) and Plate III, Fig. 2.

In the light of other experiments to be referred to later on this transformation may well be considered the beginning of a scrotum, which, however, does not develop further because in the absence of the testes no necessity or force exist toward further development.

A further hormone of the sterol type used in this investigation was progesterone, a substance which is mainly concerned with the progestational changes of the uterine endometrium. The action of progesterone on the pouch of the non-castrated normal female resembles that of testosterone, though the relaxation of the pouch seems to be even more pronounced. No castrated animal so far has been treated with progesterone.

A reaction entirely different from those obtained by the administration of œstrogens or androgens is observed after the administration of gonadotropin obtained from human pregnancy urine. This hormone which closely resembles the luteinizing factor of the anterior lobe of the pituitary, brings on a marked expansion of the marsupium following a preliminary short-lived contraction (Bolliger, 1942*c*). Even after a single injection the enlargement of the pouch may be as much as tenfold, and persists for about a week and then slowly involutes over a period of one to two months. As is well known, large amounts of this gonadotropin are excreted in the urine of human beings at the beginning of pregnancy. The purpose or the reason for this excretion is not yet clear, but it is remarkable that the marsupial apparently requires gonadotropin or a similar substance immediately before and at the beginning of pregnancy in order to condition the pouch for its important function in the process of reproduction.

Reaction of the Scrotum to Sex Hormones.

In the adolescent and adult female possum certain actions of œstrogens, androgens, progesterone and gonadotropin can be strikingly observed in the pouch of the intact animal. The action of these hormones on the scrotum of the male is also marked and similar in many respects, and has been referred to on several occasions (Bolliger and Carrodus, 1940 ; Bolliger and Canny, 1941 ; Bolliger, 1942*a* ; Bolliger and Tow, 1946). Of the hormones tested the œstrogens gave the most dramatic response. They brought on what is called testicular ascent, that is to say, the testes, permanently and irreversibly located in the scrotum, left their position and became situated under the abdominal skin.

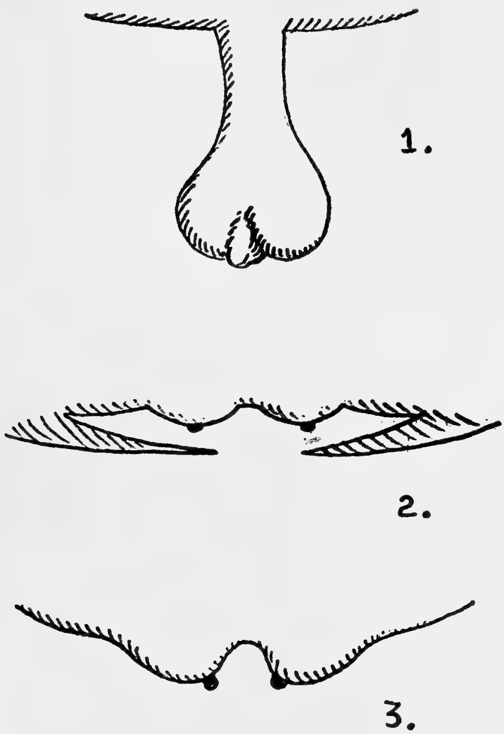

Fig. 1.—Diagramatic drawing of (1) normal scrotum of *Trichosurus vulpecula* ; (2) cross-section through normal pouch at the level of the nipples ; and (3) the appearance of the pouch in cross-section in a castrated female which has been treated with testosterone propionate.

This alteration of the position of the testes is only a temporary one, and after two or more weeks they again return into the scrotum. During the period of testicular ascent the scrotum contracts into a heap of wrinkled tissue and skin folds appear on the left and on the right of the scrotum, suggesting the formation of a rudimentary pouch. A real permanent pouch, however, was finally obtained by the repeated administration of œstrogens to castrated adolescent males. The empty scrotum became completely inverted, simulating a marsupium as is seen in the female (Fig. 1 (1) and (2)). This transformation of the scrotum into a pouch definitely proves the homology of the two organs and the lips of the pouch consequently must represent the labia majora of higher mammals according to

the accepted claim that scrotum and labia majora are homologues. Thus the embryological origin of the pouch has definitely been fixed and its marked response to sex hormones becomes understandable. It also becomes clear why the pouch undergoes such marked alterations in size when the breeding season of the normal female approaches, i.e. marked contraction followed by a fairly sudden expansion irrespective of the animal becoming pregnant or not. The pouch, as the analogue of the labia majora, belongs to the external genitalia, which in general respond strikingly well in marsupials to stimulation by sex hormones, as shown on other occasions (Bolliger and Carrodus, 1940 ; Carrodus, 1941). This complete and permanent transformation of a male organ, the scrotum, into a female one, the pouch, is probably the first one of its kind amongst mammals, and the surprising element again is the age at which this transformation takes place. The experiment was commenced in half-grown animals and the change over actually took place when the possum reached puberty.

It should be emphasized, however, that so far this transformation has only been attempted and accomplished in *Trichosurus vulpecula*, a diprotodont marsupial, and that further work should be undertaken to find out if this reaction is a general one in the order marsupialia or only confined to one of the sub-orders or families. The same problem applies to the reactions of accessory and sex organs in general, and undoubtedly a vast amount of work has yet to be undertaken to elucidate the question of reproduction as well as hosts of other unsolved problems connected with marsupials.

As stated at the beginning of this address, the study of the Australian fauna amounts to almost a national duty, not only for the morphologist, but for the scientist in general. This does not mean that such activities will lead to a narrow nationalistic outlook in science, because the problems involved are fundamental ones and, as shown in this paper, certain aspects of reproduction, for example, are more clear-cut in these primitive mammals than in higher developed vertebrates. The observations thus obtained lead to problems of the widest significance not only in the field of reproduction but of physiology in the general sense. This is brought out in investigations not mentioned in this address but published in the Journal of this Society dealing with the properties of the integument of *Trichosurus vulpecula*. This seemingly parochial theme, which was taken up after the observation that sex hormones have a marked effect on the pelage of the possum, led ultimately to the discovery that uric acid is an important constituent, not only of the marsupialian but of the mammalian hair in general (Bolliger and Hardy, 1944 ; Bolliger, 1945).

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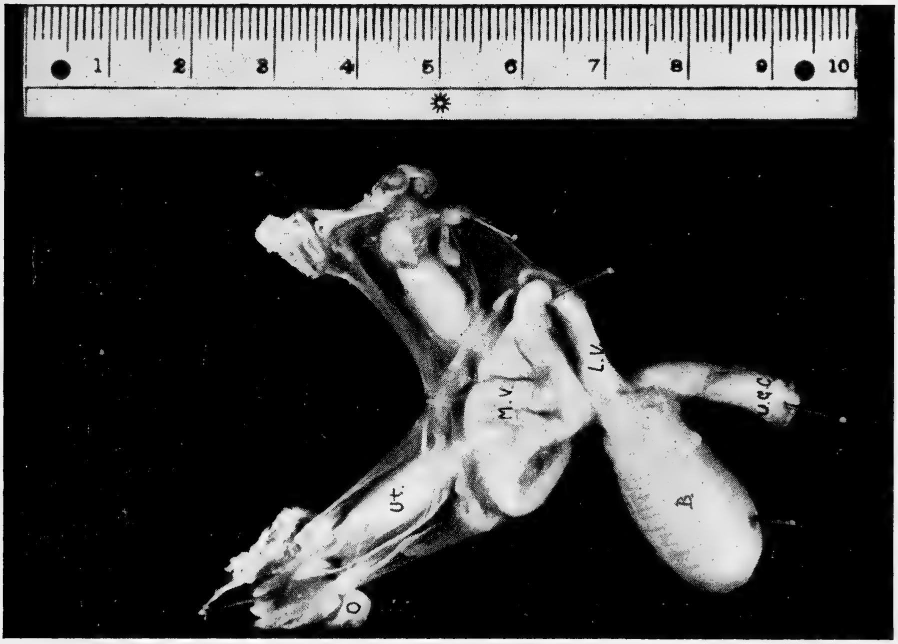

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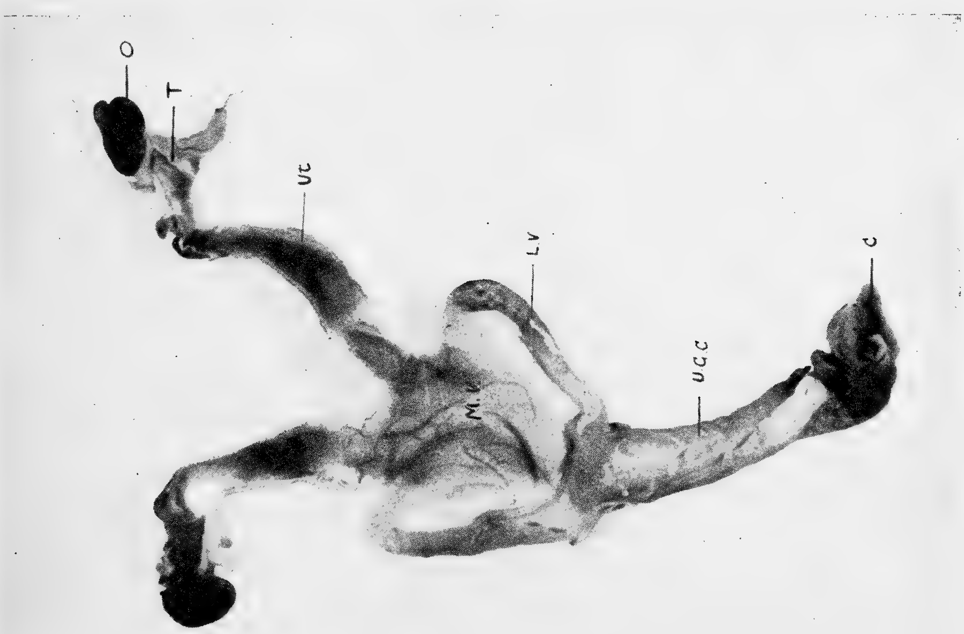

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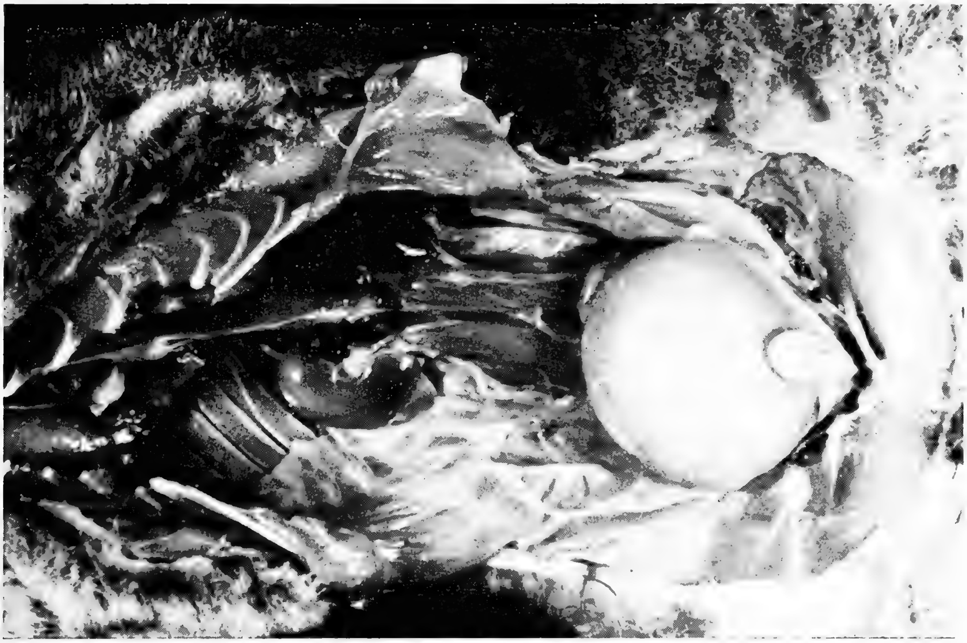

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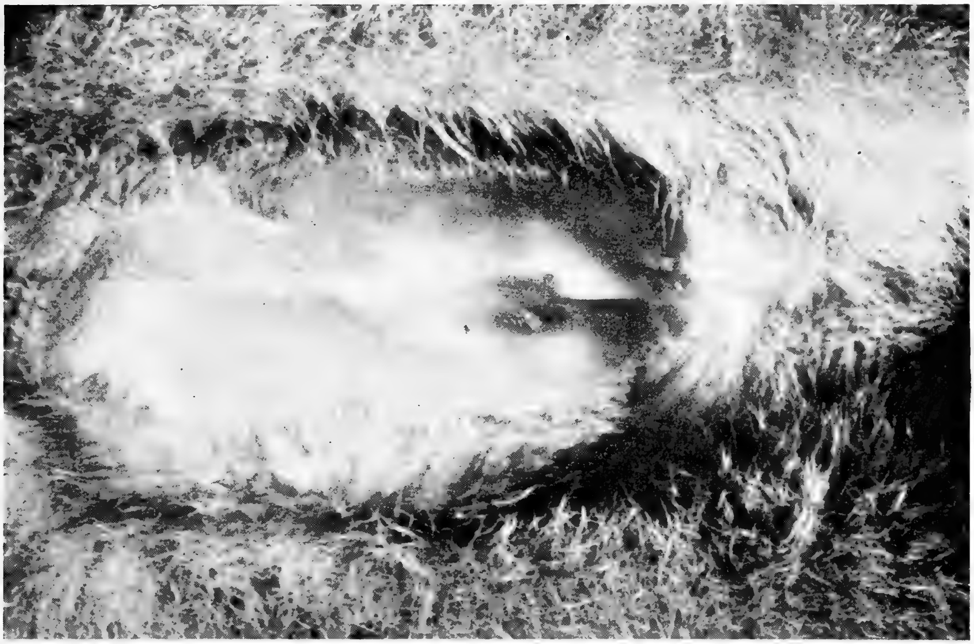

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Explanation of Plates.

Plate I.

Fig. 1.—Photograph of internal genital organs of *Trichosurus vulpecula* (untreated). O, ovary; T, tube; Ut, uterus; M.V., median vagina; L.V., lateral vagina; U.G.C., uro-genital sinus; C, cloaca. The bladder has been removed. This animal had an embryo measuring 8 cm. in its pouch.

Fig. 2.—Internal reproductive organs of adult untreated multiparous female. Bladder (B) left *in situ.*

Plate II.

Fig. 1.—Uro-genital tract of adult possum (*Trichosurus vulpecula*) which was given injections of œstradiol dipropionate weekly (0·5 mg.). Over a period of five weeks it received a total of 2·5 mg. and died four weeks later, the blood urea content being 600 mg. per cent. at the time of death. Note the enlarged median and lateral vaginæ as well as uteri. Particular attention is drawn to the markedly dilated ureters, while the kidneys are of approximately normal size. The bladder partly overlies the median vagina and is flanked by the lateral vaginæ, while the two uteri may be seen above the bladder.

Fig. 2.—Large median pyovagina obtained after the administration of a very excessive amount of œstrogen (30 mg.). The animal died 39 days after beginning the injections. The urea content was 135 mg. per cent. at death. This is the largest pyovagina produced so far following the administration of œstrogens. The relatively small bladder may be seen anteriorly at the base of the large, almost spherical, median vagina. Extending laterally from the base of the bladder may be seen portions of the right and left lateral vaginæ, represented in the photograph as two white tubes.

Plate III.

Fig. 1.—Median vagina of enormous dimensions obtained after the administration of 233 mg. of testosterone propionate, over a period of 164 days. The animal was killed after this period and the urea content of the blood did not deviate appreciably from normal. The uteri were also tremendously enlarged. Compare the median vagina and uteri with the kidneys, which are of normal size. The lateral vaginæ cannot be seen in this illustration.

Fig. 2.—Photograph of pouch region of a female which had been castrated in the state of adolescence. Subsequently, this animal had been treated with large amounts of testosterone propionate. Note the fully exposed nipples due to the complete eversion of the pouch. The appearance of the lower abdominal wall suggests the formation of a rudimentary scrotum. This structure persisted in the mature animal and was more marked when the possum was on its feet.

DEEP FOCUS EARTHQUAKES, 1909-1912.

By D. J. K. O'Connell, S.J., M.Sc., D.Ph.

Manuscript received, January 7, 1946. Read, April 3, 1946.

The latest and most complete study of the depth and distribution of deep focus earthquakes is contained in a series of papers by Gutenberg and Richter (1938, 1939, 1941, 1945). These authors give epicentres, depths and origin times for 824 deep shocks between 1905 and 1943. Their work is based mainly on the data given in the International Seismological Summary and is considered to include all important shocks from the beginning of the Summary in 1918 up to the end of 1934. A number of selected shocks after 1934 has been added. For the years before 1918 only fourteen shocks are given, and for the period 1909-1912 only two shocks. For a study of deep focus earthquakes it is obviously desirable to extend the list of epicentres if possible. It is only a few years since the existence of deep focus shocks was definitely established, and only very recently have good tables been available for the travel times of waves for deep shocks. Important phases, which an experienced observer would now recognize and report, may easily have been overlooked by earlier workers. Thus, while early bulletins are still of use, and such phases as pP and sS may sometimes be identified from them, much more satisfactory results can be obtained from a re-examination of the original seismograms. The writer accordingly set to work to analyse anew the early Riverview records in order to detect and study the deep focus earthquakes.

A Wiechert 1,000 kg inverted pendulum seismometer (NS and EW components) started recording at Riverview in March, 1909, followed by a Wiechert 80 kg vertical seismometer in April, 1909 (cf. Pigot, 1909), and by two Mainka 500 kg horizontal pendulums (NS and EW) in April, 1910. Three Galitzin seismographs were added much later, after the period dealt with in this paper. It is believed that a complete record of earth movements has been obtained from the start, apart from one break of three days in October, 1914, due to illness of the staff. Before the Wiechert vertical was installed, there were short daily gaps while the records were being changed. Since that time, while records were being changed, or adjustments made, on one instrument, the others were recording.

The vast majority of deep focus earthquakes, and all the very deep ones, occur near the margin of the Pacific basin—in South and Central America on the eastern side of the Pacific, and from the Kuriles to the Dutch East Indies and on to New Zealand on the western side. The Riverview records are particularly well suited for a study of the deep focus earthquakes of the SW Pacific. From New Guinea to the Solomons and on to Fiji and New Zealand the epicentres of these deep shocks are between 20° and 33° distant from Riverview. At these distances the characteristic phases of deep focus earthquakes are likely to be particularly clear on the records.

These early Riverview records are all the more important owing to the lack of other adequately equipped seismological stations in this part of the world. During the period dealt with in this paper, and for many years afterwards, the only other up-to-date seismographs within 3,000 miles of Sydney were those at Apia (1,000 kg horizontal Wiechert and 80 kg vertical Wiechert). Within

5,000 miles of Sydney the only other well equipped stations were those at Batavia (1,000 kg horizontal Wiechert), Manila (1,000 kg horizontal Wiechert, from April, 1911), Osaka (Omori horizontal), and Zikawei (1,000 kg horizontal Wiechert, from March, 1909). Of these stations the only ones with vertical components were Apia and Riverview.

All the Riverview records were examined. Those that appeared to be of deep focus were reanalysed. Usually the depth could be determined from the records. All available reports from other stations were used in checking the depth and in determining the epicentre and magnitude of the shock. There is a fairly good, though not quite complete, collection of seismological bulletins at Riverview. In order to convey an idea of the material used, the available bulletins for the period 1909-1918 are listed in Table 1. In some cases readings from other stations were found here and there in the literature.

TABLE I.

Apia	1907-13, 1917	Helwan ..	1910+	Riverview ..	1909+
Baku	1910	Innsbruck ..	1913-15	St. Louis ..	1910-15
Balachany	1910	Irkutsk ..	1913	San Fernando	1910+
Batavia ..	1910+	Jena ..	1905-12	Santa Clara	1911-16
Budapest ..	1911-12	Ksara ..	1911-14	Santiago ..	1909, 1913-15
Cartuja ..	1909-16	Laibach ..	1912-14	Sarajevo ..	1912-13
Catania ..	1910-15	La Paz ..	1914+	Stonyhurst	1909+
Christchurch	1909-11, 1915	Lemberg ..	1912-17	Strasbourg ..	1910-14
Cleveland ..	1911-16	Manila ..	1908+	Tiflis ..	1913, 1915
Cracow ..	1913-17	Marseilles ..	1912+	Tortosa ..	1910+
Czernowitz ..	1913-14	Mungret ..	1913	Trieste ..	1912-17
Darmstadt ..	1911-14	Nagasaki ..	1913	Uccle ..	1910+
De Bilt ..	1908+	Osaka ..	1909+	Upsala.. ..	1917-18
Frankfurt a. M.	1913	Ottawa ..	1908+	Valetta ..	1914-17
Georgetown ..	1915+	Padua ..	1910-15	Valle di Pompeii	1914+
Göttingen ..	1903-14	Paris ..	1915+	Vienna ..	1909-17
Graz ..	1909+	Pola ..	1912-17	Wellington	1909-11
Hamburg ..	1908-13, 1915	Reykjavik	1910	Zagreb ..	1913-14
Harvard ..	1911+	Rio de Janeiro ..	1906+	Zikawei ..	1908+

British Association Seismological Committee. Circulars 1909-12.
British Association Seismological Committee. Bulletins 1913-17.
French stations, 1910-19 (Bur. Cent. Mét. de France. *Bull. Sismologique*).
Indian stations, 1910-13 (*Monthly Weather Review, India*).
Italian stations, 1910-13, 1917-19 (*R. Ufficio di Meteorologia e Geofisica*).
Russian stations, 1911 (*Acad. of Sci., Comm. Cent. Sismique Permanente, Bull.*).
Swiss stations, 1916+ (*Schweizerischer Erdbebendienst*, Zürich).

The data from Apia, Batavia, Manila, Osaka, Riverview and Zikawei were naturally the most important for the SW Pacific earthquakes. Some of the European stations were helpful, both in checking the depth of focus and in determining the epicentre and the magnitude. The very detailed Jena bulletins were particularly useful. Unfortunately, they were not available after August, 1912, which was the last bulletin to arrive before World War I. There were, unfortunately, extremely few good stations in North or South America. The great development of seismology in the U.S.A. came at a later period.

Depth of Focus.

The depth of focus was determined in most cases from the intervals P–pP and S–sS for the nearer stations, and from P′–pP′ and PP–pPP for the distant stations. ScS and SKS and other phases were sometimes used. The tables used were those of Jeffreys and Bullen (1940), supplemented by those of Gutenberg and Richter (1936*b*).

Epicentres.

The epicentres were determined by a graphical method described by Gutenberg and Richter (1937, p. 178). If a and b are two points on the earth's surface not more than a few degrees apart, and if $\triangle_a$ and $\triangle_b$ are the distances from them to a third point c, then, if $\triangle_b - \triangle_a$ is plotted as ordinate against the azimuth of c from a as abscissa, for various values of c, the points will lie on a sine curve. The amplitude of the curve gives the distance from a to b, and the turning points of the curve give the azimuth of the line ab, so that, if the position of a is known, that of b can be obtained from the graph.

An approximate epicentre was first obtained. In nearly every case it was possible to find in the I.S.S. an epicentre not far from this position. The I.S.S. epicentre was then taken as the point a. This saves a good deal of time, as distances and azimuths had then to be computed only for those stations not given in the I.S.S. Geocentric distances were used throughout. The distances in the I.S.S. were reduced to geocentric distances by means of Bullen's tables (1938). The differences between these calculated distances and the observed distances (obtained from the arrival times of P and other waves, using an assumed origin time) were plotted against the respective azimuths. A sine curve was fitted to the points, and the distances and azimuth of the epicentre from the provisional one were found from the graph. The origin time was corrected when necessary by the aid of the graph.

The available material was hardly sufficient to justify the labour of least square solutions. This graphical method gives as accurate a result as could be expected. It has the advantage of showing at a glance any discordant observation.

Magnitude.

Only very recently has it become possible to estimate the magnitude of an earthquake from the observed ground movement at seismological stations. After much preliminary work, satisfactory methods have been evolved by Gutenberg and Richter. Details are given in papers by Richter (1935), Gutenberg and Richter (1936*a*, 1942) and Gutenberg (1945*a*, 1945*b*, 1945*c*). Their magnitude scale is partly empirical, partly based on theory. It ranges from 0 (the smallest shocks recorded) to $8\frac{1}{2}$ (the greatest magnitude found by them for shallow earthquakes). Gutenberg and Richter (1942) find that, if E is the total energy (in ergs) of a shallow earthquake and M its magnitude, then

$$\log E = 11 \cdot 3 + 1 \cdot 8\, M \qquad (1)$$

It follows that the energy of an earthquake of magnitude M is 60 times that of an earthquake of magnitude M–1, while magnitude 0 corresponds to an energy of about 10^{11} ergs and magnitude $8\frac{1}{2}$ to 4×10^{26} ergs. The importance of this work for various branches of seismological research is evident. It will certainly bear much fruit in years to come.

Magnitude determinations for deep focus earthquakes present special difficulties, which have at last been overcome. The method of determining the magnitudes of deep focus earthquakes from the amplitudes of P, PP and S is contained in a paper by Gutenberg (1945*c*) just received. He defines the magnitude of deep focus earthquakes by equation (1), originally derived for shallow earthquakes. Graphs and tables are given for computing from the observed ground movements the magnitude of shocks at different depths and epicentral distances. Gutenberg's methods have been followed strictly. The magnitude of each shock was calculated for every P, PP and S that could be identified on the Riverview records or in the bulletins of other stations. The station corrections given by Gutenberg were applied. Comparatively few stations reported earth amplitudes, and many of those gave only the

amplitudes of surface waves. The stations used for obtaining magnitudes were Apia, Batavia, Manila (from August, 1911), Osaka (from 1911), Riverview, Zikawei (from 1912) and a number of European stations, Göttingen, Graz, Hamburg, Jena, Strassburg, Vienna, also at times Ottawa and Reykjavik. The Riverview amplitudes were usually taken from the Wiechert instruments, occasionally from the Mainkas. The constants of the seismographs are determined monthly. Except when alterations are made deliberately, the constants do not change much from month to month, and it is believed that they are reliable.

The results are given in Table II. The origin time in column 3 is given in Universal Time (GMT from midnight). The depth of focus in column 4 is the depth below the surface of the earth. The epicentre in column 5 is given to

TABLE II.

No.	Date.	Origin. U.T.	Depth.	Epicentre.	No. of Stations.	Quality.	Mag.	No. of Stations.
	1909	h. m. s.	km.	° °				
1	May 2	6 56 50	100	19 S. 171½ E.	23	C	6·6	4
2	,, 2	18 11 10	100	19 S. 171½ E.	18	C	6·5	3
3	Aug. 18	00 39·6	100	21½ S. 170½ E.	27	B	7·2	4
4	Nov. 10	06 13·6	160	32½ N. 131½ E.	41	C	7·6	7
5	Dec. 9	23 28·9	100	12½ N. 145 E.	35	C	8·0	5
	1910							
6	Feb. 4	14 00 22	100	21½ S. 170½ E.	57	B	7·0	5
7	,, 4	14 40 34	100	21½ S. 170½ E.	16	C	6·8	3
8	,, 4	17 37 01	100	21½ S. 170½ E.	36	B	6·8	4
9	,, 4	18 33 02	100	21½ S. 170½ E.	22	C	6·5	3
10	,, 12	18 10 07	350	33 N. 138½ E.	42	B	7·6	4
11	Apr. 12	00 22 11	160	25 N. 123 E.	70	C	7·8	7
12	,, 20	22 22 02	480	21½ S. 175½ W.	31	C	7·1	3
13	Aug. 21	05 38 32	550	18 S. 178½ W.	53	B	7·4	5
14	Nov. 15	14 21 40	100	58 S. 23 W.	53	C	7·3	3
15	,, 29	11 45·4	500	7 N. 123½ E.	8	C	6·8	1
16	Dec. 14	20 46 00	600	21½ S. 175½ W.	46	C	7·4	4
	1911							
17	Mar. 6	17 30·0	100	6 N. 126½ E.	28	C	6·5	1
18	Apr. 1	02 02 39	550	18 S. 179 W.	29	B	6·8	3
19	,, 28	18 35·8	670	28½ S. 179½ E.	23	C	6·0	2
20	May 4	23 37 01	200	52½ N. 157½ E.	89	B	7·5	10
21	June 15	14 25 59	160	28½ N. 128 E.	97	B	8·4	8
22	July 3	21 45 30	670	4 S. 122 E.	27	B	6·8	3
23	,, 5	18 40 06	320	7½ S. 117½ E.	48	B	7·0	4
24	,, 11	21 22·3	160	14½ S. 67½ E.	51	C	7·3	4
25	,, 19	10 00 50	160	30 S. 177½ W.	58	C	7·2	4
26	Aug. 21	16 28 57	350	21 S. 175½ W.	54	C	7·4	4
27	Sept. 12	12 53 11	150	23 S. 174 E.	32	D	6·9	2
28	Oct. 20	17 44·1	200	12 S. 166½ E.	59	B	6·8	7
29	Nov. 22	23 05·4	200	15½ S. 168½ E.	56	B	7·2	5
	1912							
30	Mar. 25	04 49 27	220	19 S. 170 E.	29	C	7·2	2
31	May 15	00 04 18	220	30 S. 177½ W.	43	C	6·5	3
32	Aug. 6	21 11 20	220	14 S. 167 E.	68	B	7·2	5
33	,, 18	13 20·0	670	6½ S. 123½ E.	16	C	7·0	2
34	,, 19	16 21·9	150	11½ S. 167 E.	31	C	6·7	2
35	Sept. 1	04 10 02	410	4½ S. 154½ E.	47	B	6·9	5
36	,, 17	18 51·6	600	23½ S. 178½ W.	16	D	6·3	2
37	,, 29	20 51·5	70	7 N. 137 E.	67	C	7·4	2
38	Oct. 26	09 00 36	100	15 N. 146 E.	34	B	7·1	5
39	Nov. 7	07 40 24	100	57½ N. 153 W.	76	B	7·1	6

the nearest half degree. In column 6 is given the number of stations whose readings were available. This number is a rough indication of the size of the shock, compared with others in the same region, at the same depth, and not so distant in time that there would be a significant change in the number of observing stations or in their equipment. It is not, however, an indication of the reliability of the epicentre, for many of the stations were of inferior quality. In many cases more accurate results were obtained with comparatively few stations, partly because the reports from these stations were more reliable, partly owing to a favourable distribution of the stations in azimuth, and partly due to the nature of the shock itself.

In column 7 an attempt is made to assess the accuracy of the determination of the epicentre. The letter indicates the quality as follows:

A. Very accurate (probable error of a few tenths of a degree).

B. Good (epicentre not likely to be in error by more than one degree).

C. Fair.

D. Poor.

The accuracy depends on the number of good stations reporting the shock, on their distances and distributions in azimuth, and on the sharpness of the impulses. Quality A was chosen as that of a really good modern determination. None of the epicentres given here quite reached that level. That was to be expected, seeing that (1) the number of good stations was much less than nowadays; (2) they were less well distributed; (3) times in general were less accurate.

The magnitude is given in column 8. In column 9 is given the number of stations used in determining the magnitude.

All the deep focus earthquakes detected on the Riverview records, for which epicentres could be determined, are given in the table. For the SW Pacific region the list is probably fairly complete for shocks above certain limiting magnitudes. When more material has been obtained, it may be worth while to estimate these limiting magnitudes for shocks in a particular region at a given depth. No attempt has been made to make a complete catalogue of shocks in more distant regions. That could be done much more satisfactorily by studying the records of stations nearer to those regions.

The only very deep shock found on the records and not given in the table is one on September 11, 1912. From the Riverview records the depth is estimated as 670 km, distance from Riverview 36°, origin time 19h 43·4m (UT), magnitude $6\frac{1}{2}$. The only other stations reporting the shock are Batavia and Manila. The epicentre is in the region of 9° S. 121° E. An examination of the Batavia records might give further information. Unfortunately the Manila Observatory and all its valuable records have been destroyed.

On November 12, 1912, there were two shocks, evidently both from the same epicentre. The first was recorded only at Riverview, the second was reported also by Batavia and Manila. The epicentre is in the region of 23° S, 173° E. From the Riverview records the depths of the two shocks are estimated as 160 and 190 km respectively; origin times, 4h 40·6m and 15h 11·6m (UT); magnitude of each, $6\frac{1}{2}$.

Nearly all the epicentres in the table fall within the zones covered by the deep focus shocks studied by Gutenberg and Richter and shown in their charts (Gutenberg and Richter, 1945). The exceptions are Nos. 14, 35, 37 and 39, which are in new regions or in extensions of the Gutenberg-Richter zones. The magnitude, 8·4, found for No. 21, is slightly greater than the greatest magnitude, $8\frac{1}{4}$, so far found by Gutenberg for a deep focus shock (Gutenberg, 1945*c*, p. 129).

The author is greatly indebted to Professor B. Gutenberg for his advice and for the generous loan of unpublished material.

Summary.

With the aim of extending the material available for the study of deep focus earthquakes the author re-examined the early records of the Riverview seismographs. All the shocks that could be identified as being of deep focus were analysed. With the aid of all available reports from other stations, epicentres, depths and origin times were obtained for 39 shocks from March, 1909, to the end of 1912. Magnitudes were determined by Gutenberg's method.

The catalogue should be fairly complete for the SW Pacific zone, at any rate for the deeper shocks of at least moderate intensity.

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A SIMPLE DEMONSTRATION OF FILM AND NUCLEAR BOILING.

By R. C. L. Bosworth, D.Sc., F.Inst.P.

Manuscript received, April 11, 1946. Read, May 1, 1946.

When a liquid is caused to boil on a hot solid surface maintained at a temperature θ above the boiling point of the liquid concerned, the magnitude of the rate of heat transfer or emittance (q) in units of heat per unit area per unit time, varies in a peculiar manner with θ. When the temperature of the hot surface is only slightly in excess of the boiling point the vapour formed breaks away from the surface in a series of discrete bubbles leaving a continuous film of liquid in contact with the hot solid. This has been designated nuclear boiling. At a certain temperature the vapour in the act of breaking away from the surface forms a continuous sheet or film. Owing to the much lower thermal conductivities and convection moduli of vapours as compared with liquids, the emittance q and the associated rate of boiling decrease abruptly as soon as the condition of film boiling sets in.

A typical plot of q versus θ is shown in Figure 1.

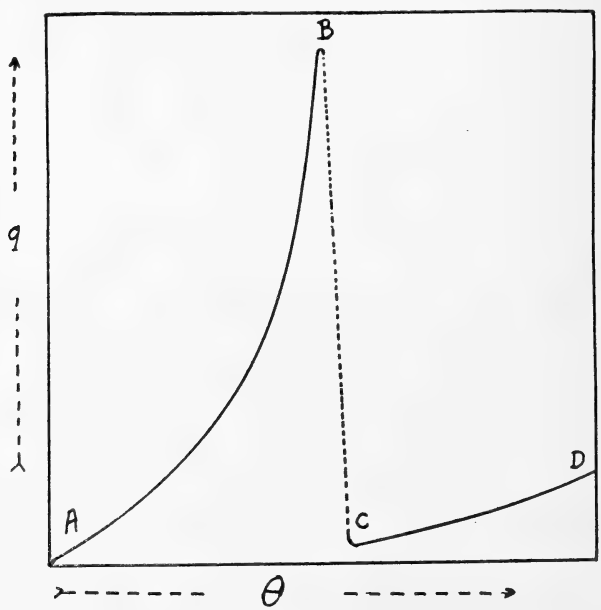

Fig. 1.

The phenomenon represented by Figure 1 is of industrial chemical importance in that its occurrence sets a limit to the economic capacity of an evaporator or still with a given heating surface. From conditions represented by point A to those represented by point B an increase in the temperature of the heating surface will produce an increase in the rate of boiling, but a further increase in

the temperature of the heating surface results in a serious drop in the rate of boiling.

From A to B nuclear boiling occurs and over this range the emittance increases rapidly with increase in θ. Beyond B film boiling sets in and the emittance drops to a very much lower value at C. With still further increase in the temperature of the hot surface the value of q rises slowly and steadily from C to D.

The change over from nuclear to film boiling is only abrupt if the surface is relatively clean and smooth. The effect of surface roughness, scale or chemical films is reviewed in reasonable detail by McAdams (1942). We are concerned here only with the behaviour of clean and smooth surfaces which may easily be realized and the two types of boiling readily demonstrated by utilizing the fact that a copper block heated to dull redness and dropped into liquid alcohol or methylated spirits will, provided too heavy an oxide layer has not been allowed to form on the specimen, be rendered clean and bright, and boiling on the surface will proceed according to the film mechanism. As the specimen cools the rate of boiling decreases until we come to a temperature corresponding to the point C on Figure 1. Nuclear boiling now sets in. There is a great increase in the rate of boiling which may become quite violent if a large specimen is used. At the same time the rate of cooling is greatly accelerated with the result that the temperature of the specimen now rapidly falls below the boiling point.

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VOLUME LXXX

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PHYSICAL CHANGES ACCOMPANYING DRYING OF SOME AUSTRALIAN LIGNITES.

By J. A. Dulhunty, D.Sc.,
Commonwealth Research Fellow. University of Sydney.

Manuscript received, May 14, 1946. Read, June 5, 1946.

Introduction.

Results described in this paper were obtained during preliminary investigations of physical changes observed to accompany the drying of certain Australian lignites—particularly those associated with sub-basaltic Tertiary silts at New Chum Hill, Kiandra, and Wullwye Creek, Berridale, on the Southern Tablelands of New South Wales.

At outcrops where seams were not decomposed by weathering, but where they had dried out from exposure to the atmosphere, woody and homogeneous lignites were black, hard and brittle, exhibiting conchoidal fracture, and a lustre nearly as bright as that of bituminous coal. At points well behind the outcrop material, where seams were permanently saturated with natural ground water, the lignite was soft, somewhat earthy, and quite dull, without any trace of the bright lustre of the outcrop material. Dried in the sun, however, it became just as hard, brittle and bright, and when soaked in water did not return to its original soft, dull condition. Pieces of yellowish-brown, woody lignite occurring in the soft, dull material became somewhat harder, developed a silky sheen when dried, and did not return to their original condition when soaked in water.

From these observations it appeared that fundamental physical changes of an irreversible nature took place when the lignites were dried in air, and that the physical changes were similar to those which take place, without drying, when the rank of coal is increased by natural processes of coalification.

Some Tertiary lignites from other localities in Australia exhibit the same changes on drying. The amorphous brown coal, forming thick deposits at Yallourn (Morwell), Victoria, remains soft and dull when dried ; but in it there are fragments of dark-coloured woody lignite which, taken from fresh working faces of the open-cut mine, become relatively hard and bright on drying, and do not return to their original soft, dull condition when placed in water.

Occurrence and Nature of Lignites Investigated.

At New Chum Hill, Kiandra, the homogeneous lignite with included fragments of woody lignite, occurs as seams in a thick bed of silt beneath Tertiary basalt flows. The basalt is considered to be of Miocene Age, and the underlying silt is probably late Oligocene or early Miocene (Andrews, 1901 ; Browne, 1933). The occurrence at Wullwye Creek, Berridale, is of the same general nature and age to that of Kiandra, although the full thickness of sub-basaltic silt is not exposed. Thickness of lignite and associated silts, and their relation to overlying basalt flows in the two localities are illustrated in Table I.

The silt beds are essentially unconsolidated, varying from stiff, puggy clay to laminated sandy clay and relatively loose sand. The sediments have not been silicified or hardened, and the lignites do not appear to have been altered by heat from the basalt flows. This is evident at New Chum Hill, where the top seam, 40

TABLE I.

Occurrence of Tertiary Lignites at Kiandra and Berridale.

New Chum Hill, Kiandra.	Feet.	Wullwye Creek, Berridale.	Feet.
Basalt flow	50–100	Basalt flow	Up to 200
Decomposed basalt	20	Gravels, sand and sandy clay	100
Basalt flow	25	*Lignite*	4
Sandy clay	40	Clay	5
Lignite (Top Seam)	4	*Lignite*	3
Coarse sand and sandy clay ..	40	Sandy clay	20
Lignite (Middle Seam) ..	6	*Lignite*	4
Coarse sand and sandy clay ..	75	Sand and clay to creek level..	6
Impure Lignite (Bottom Seam)	10		
Fine sand and shaley clay ..	60		
Palæozoic basement-rock ..	—		

feet beneath the base of the flow, is of the same general nature and rank as the lowest seam 165 feet below the basalt. It is probable that the considerable thickness of porous sediments, saturated with circulating groundwater, prevented heat from penetrating to the lignite.

The lignite seams consist of macerated plant débris forming a slightly laminated, but otherwise homogeneous, matrix in which woody lignite in the form of leaves, pieces of wood, tree stumps, and portions of tree trunks are embedded. The homogeneous material ranges from dark brown to black, and possesses the ultimate and proximate chemical compositions shown in Table II. The included fragments of woody lignite, yellowish-brown to black, show considerable variation in chemical composition—carbon increasing as the colour of the wood deepens.

TABLE II.

Chemical Composition of Lignites from Kiandra and Berridale, N.S.W.

Sample No.	Nature of Lignite.	Ash.	Prox. Comp. A.F.D.		Ult. Comp. Nit. Sul. Ash-free-dry.			N.	S.
			Vol.	F. Carb.	C.	H.	O.		
C.S.88 Berridale.	Black, homogeneous	4·9	46·3	53·7	68·7	5·1	26·2	0·5	0·6
C.S.87 Kiandra.	Brownish - black, slightly woody ..	7·2	52·5	47·5	60·6	4·9	34·5	0·6	0·8
C.S.141 Kiandra.	Yellowish - brown fibrous woody-structure ..	0·8	72·3	27·7	57·4	6·0	36·6	0·7	0·4

INVESTIGATION OF PHYSICAL CHANGES ACCOMPANYING DRYING.

The following investigations were carried out on both homogeneous and black woody lignites to determine the nature and cause of change from the original soft, dull state to the hard, bright condition when dried.

Drying in Inert Gases.

Preliminary tests were made to confirm the assumption that changes in hardness and lustre were direct consequences of removal of water, and not some form of oxidation due to reaction with atmospheric oxygen during drying.

The lignites were dried over calcium chloride in atmospheres of nitrogen, carbon dioxide, and air. They became hard and bright in each case—no difference being detected in the nature or degree of changes under different conditions. Pieces were also dried in nitrogen over concentrated sulphuric acid at room temperature, and also in a stream of dry nitrogen at 105° C. The changes in hardness and lustre were equally pronounced in both cases.

These tests indicated that changes were due to removal of water, and not reaction with gases of the atmosphere, and that temperature of drying had no apparent effect on the changes.

Irreversibility of Physical Changes.

Pieces of lignite rendered hard and bright by drying in nitrogen at room temperature were soaked in cold water for a period of three months; boiled in water at atmospheric pressure for 60 hours; treated with steam at 50 lb. per sq. in. and 150° C. for 70 hours; and heated in water 150° C. under 50 lb. per sq. in. for 60 hours. In all cases the hard, bright nature of the materials persisted; and it was concluded that the changes could not be reversed.

Replacement of Water with Other Liquids.

Experiments were carried out to discover whether the irreversible changes were due to physical removal of "free" water, or the elimination of chemically combined water, such as hydroxyl groups, from the organic molecules.

Granular samples of the soft, dull, water-saturated lignites were placed in absolute alcohol, and water was extracted by changing the alcohol ten times (once every third day). They remained soft and dull. Small pieces taken from each of the samples and dried in nitrogen over concentrated sulphuric acid became hard and bright. The changes were irreversible as they persisted when the materials were saturated with alcohol or water.

After extraction of water with alcohol, those portions of the samples which had not been dried were placed in petroleum ether (B.P. 40–60° C.), and alcohol was removed by changing the petroleum ether ten times (once every third day). The lignites became slightly harder, but remained dull. Small pieces, dried in nitrogen over concentrated sulphuric acid, became hard and developed a bright lustre—a little less brilliant than when dried from alcohol. They remained hard and bright when soaked alternatively in water, alcohol and petroleum ether.

The extent to which water had been removed during treatment with alcohol and petroleum ether was tested as follows: Dry nitrogen was bubbled through petroleum ether, and then passed through a calcium-chloride tube until the weight of the tube was constant. Pieces of lignite, saturated with petroleum ether after removal of alcohol, were heated at 105° C. for two hours in a U-tube to which the weighed calcium chloride tube was connected, while a stream of dry nitrogen was passed over the lignite and through the calcium-chloride tube. Increase in weight of the calcium-chloride tube represented 0·3% of the dry weight of lignite in the U-tube, indicating that removal of water had been almost complete during treatment with absolute alcohol, as the lignites originally contained about 60% of water.

During treatment with alcohol and petroleum ether, small quantities of substances were dissolved from the lignites, producing slight coloration of the liquids, and a faint blue fluorescence. A test was made to determine the effect of this on the physical changes. Lignite was treated with alcohol and with petroleum ether in the manner already described. It was then brought back to

the water-saturated condition by removing petroleum ether in successive changes of alcohol, and finally replacing alcohol with water. At this stage it was as soft and dull as before removal of original water. When dried it became hard, developed a bright lustre, and could not be distinguished from lignite dried from the original water-saturated condition. This indicates that the removal of small quantities of soluble substance has no effect on the physical changes accompanying drying, and that the ability to undergo the irreversible physical changes is not impaired by exchange of liquids, providing the lignite is not allowed to dry.

The foregoing results show that similar irreversible physical changes take place when the lignites are dried from water, alcohol and petroleum ether. It is possible that alcohol, in replacing water, may take the place of hydroxyl groups attached to organic molecules; but this would be impossible in the case of the paraffin molecules of petroleum ether. Thus, it appears that the changes are a direct consequence of physical removal of liquid, and not chemical changes such as loss of hydroxyl groups. Bangham (1943) suggested that humic acid molecules aggregated into colloidal particles or micelles, may be arranged with their non-polar parts directed inwards, and their polar groups turned outwards to remain associated with ions of soluble salts in the watery medium. Under these conditions, removal of water may result in reorientation of molecules at the surface of the micelles. Such effects, however, do not appear to be connected with changes in hardness and lustre, as the changes occurred when the lignites were dried from petroleum ether after removal of water.

Relations between Physical Changes and Removal of Water.

Removal of water was carried out in progressive stages to determine relations between development of irreversible physical changes and reduction of water content in the lignites. They were brought into equilibrium with atmospheres of successively lower relative humidity; moisture content was determined at each; changes were noted in physical properties; and their permanency was tested. Atmospheres of different relative humidity were obtained in desiccator jars filled with nitrogen, and charged with aqueous solutions of sulphuric acid of varying concentration calculated to give required humidities. Small pieces (about $\frac{1}{4}$ in. cubes) of black homogeneous lignite (kept water-saturated after sampling) were placed in each of the jars, and air replaced with nitrogen. Eight weeks was allowed for the lignite to reach equilibrium, the temperature of the jars being maintained between 20 and 25° C. The moisture content of the material in each jar was then determined by transferring several pieces to a weighed U-tube filled with dry nitrogen. The tube was re-weighed and then heated at 105° C., a stream of dry nitrogen being passed until moisture was removed, and the weight was constant. This required about $1\frac{1}{2}$ hours. The moisture content of the material at different relative humidities was calculated to the sulphuric-acid-dried basis.

Development of hardness and bright lustre at different stages during drying, and the extent to which the changes were irreversible were determined by examining fragments not used for moisture determinations. In each case degree of lustre was noted; hardness and tenacity were examined by crushing on glass with a spatula; and permanency of the changes was tested by immersing in water for seven days.

Figure 1 shows the curve (A) obtained for reduction of moisture content in the lignite, with decreasing relative humidity under the particular conditions of the experiment which involve drying from the original water-saturated condition. Moisture content at 100% relative humidity is the maximum inherent moisture determined by Dunningham's blotting paper method (Dunningham, 1943).

Only small amounts of moisture were removed at humidities above 90%. Between 90% and 80%, almost half the total water was lost, after which the rate of removal decreased until about 20% humidity was reached. It then commenced to increase slightly as the dry condition was approached. Above 90% humidity only slight changes were noted in hardness and lustre, and the lignite returned to its original condition when soaked in water. Between 90% and 80% it became hard and bright, and the changes remained when it was immersed in water. Below 80% it became somewhat more brittle, but there was no further change in lustre. It was concluded that the irreversible physical changes occur between 90% and 80% humidity, where large amounts of water are lost, and the drying-curve is almost horizontal.

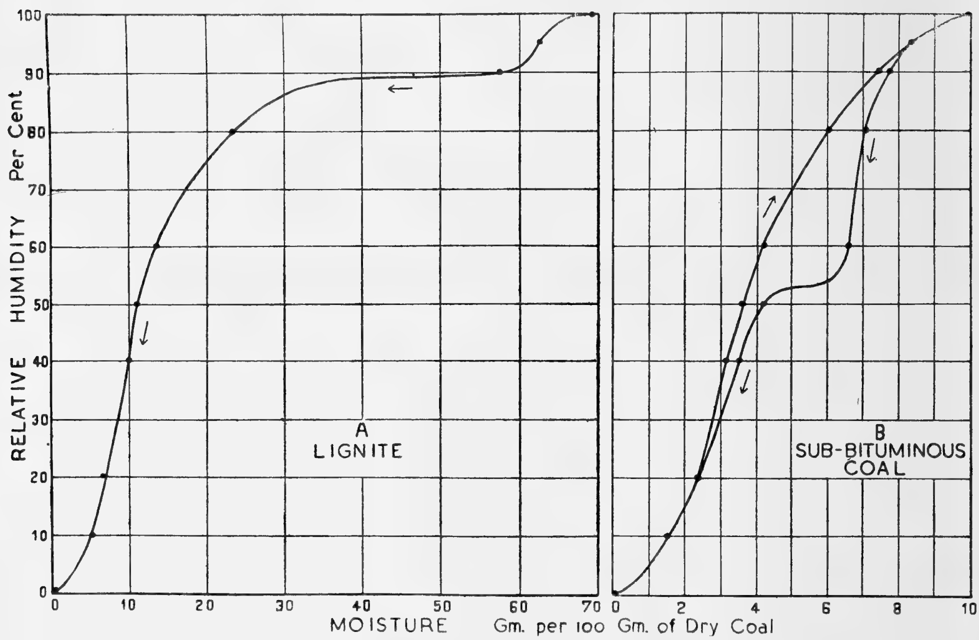

Fig. 1.

Coal sorption diagrams, consisting of both desorption and adsorption curves, show a typical hysteresis effect, most pronounced at humidities between 40% and 70% (Porter and Ralston, 1916 ; Gauger, 1932 ; King and Wilkins, 1943). During desorption the coal contains more moisture than it does during adsorption at the same relative humidities. King and Wilkins have shown that the desorption curves for English coals of bituminous rank exhibit a sudden change in slope at about 50% humidity, the curves becoming relatively flat as large amounts of water are lost for small changes in humidity. They point out that this section of the desorption curve corresponds to the stage at which a large number of capillaries of about the same size are emptying.

The hysteresis effect and change in slope of the desorption curve are illustrated by the sorption curves in Fig. 1 (B), obtained for a sub-bituminous Jurassic coal from Boomley, N.S.W. The change in slope occurs between 50% and 60% humidity, which is somewhat higher than in the more mature English coals examined by King and Wilkins. The humidity where the change in slope occurs is related to the size of the capillaries which are emptying. As the capillary sizes or inter-micelle spaces become larger, so the humidity at which

they empty will increase. In the lignite drying curve, the flat section occurs at high humidities (90% to 80%), suggesting a high proportion of relatively large inter-micelle spaces. The irreversible physical changes in hardness and lustre also take place between 90% and 80% humidity, while the large spaces are emptying. Thus macroscopic physical changes and sorption phenomena can be related in terms of micelle structure.

It has been shown by X-ray diffraction and other methods that soft, immature coal is of the nature of a gel or colloidal suspension of organic micelles in a watery medium, and that the micelles grown by self-aggregation during the maturing process, finally coalescing and expelling the fluid medium (Bangham, 1943 ; Hirst, 1943).

In the present case it is probable that the lignites had reached a critical stage in rank advancement where the micelles had grown until they were just touching with very small contact areas, and that removal of water by drying, allowed surface attraction of van der Waal's forces to deform the micelles, greatly increasing the contact areas, and reducing intervening spaces. Under these circumstances, increase in hardness and development of bright lustre would probably be due to formation of a fine, homogeneous structure and reduction of internal surface. Increase in contact area between the micelles would considerably increase the cohesive forces holding them together. This would probably account for the irreversible nature of the physical changes on drying, as the internal pressure of adsorbed water would not be sufficient to overcome the increased cohesive forces.

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THE INSTABILITY CONSTANT OF THE TRIS-ORTHOPHENANTHROLINE FERROUS ION.

By F. P. Dwyer, D.Sc.
and R. S. Nyholm, M.Sc.

Manuscript received, May 8, 1946. Read, June 5, 1946.

The determination of the instability constant of the tris-orthophenanthroline ferrous ion was undertaken at the suggestion of Dr. Adrien Albert in order to ascertain the concentration of free ferrous iron in biological fluids containing orthophenanthroline.

The free base (I) acts as a powerful chelate group and yields cationic complexes with Fe^{II} and Fe^{III} (Blau, 1888, 1889), Cr^{II} and Cr^{III} (Hammett, Walden and Chapman, 1934), and Cu^{I} and Cu^{II} (Tartarini, 1933). Other common metallic ions also react but the complexes have not been extensively studied except for resolution experiments.

The most notable effect of chelation with orthophenanthroline is that the lower valency state of the metal is highly stabilized. This is indicated by the redox potentials of the complexes compared with the free ions (shown in brackets): $Fe(o\text{-phen.})_3$: $1\cdot06$ ($0\cdot77$), $Cr(o\text{-phen.})_3$: $0\cdot7$ ($-0\cdot41$). It follows therefore that the concentration of the free ion falls to an extremely low value upon complex formation.

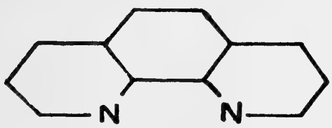
The determination of instability constants of complexes resolves into the determination of small concentrations of the free simple ions in solution containing a known excess of the complex forming substance. Four common methods are available:

(1) The Polarographic method depends on the measurement of the concentration of an electro-reducible ion at a dropping mercury electrode, by measuring the diffusion current at a polarized electrode. From the shift in the height of the polarogram in passing from a molar concentration "c" of the simple ion to the same concentration of the complex ion the diminution in concentration of the simple ion can be estimated. From a knowledge of the concentration of the free coordinating agent in the solution the instability constant can be determined. Like all polarographic determinations this method is limited to substances reduceable at a mercury surface.

(2) Addition to the complex solution of another ion in known concentration such that an insoluble compound of known solubility product is formed. This method is limited by the difficulty of ascertaining the point of incipient crystallization.

(3) A solution of the complex is used as the half cell of a concentration cell and compared with a solution of known concentration of the free ion. In the present instance this method was found impracticable owing to the rapid corrosion of the pure iron electrodes and the difficulty of obtaining ferrous salt solutions completely free of ferric salt. Although the ferric ion concentration can be reduced to a very small value by catalytic reduction with hydrogen and platinum black when the orthophenanthroline is added the concentration of ferrous ions also becomes very small. The residual concentrations of ferrous and ferric ions then become comparable and the iron electrode behaves as a redox electrode.

(4) An inert redox electrode is immersed in a solution containing the complex excess O-phenanthroline and a known concentration of the free ions of a higher valent state, and the potential determined. This method used in the present determination has the advantage that the ferrous salt solutions used to prepare the complex need not be especially free from ferric salt since the concentration of ferric ion impurity is negligible by comparison with that subsequently added. The method is practicable, however, only if the excess of orthophenanthroline does not react with the ferric salt.



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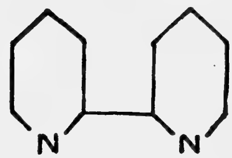
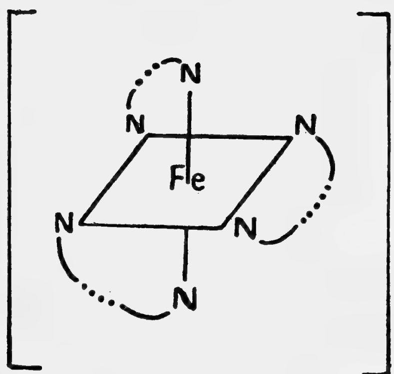


III



II

Like potassium ferricyanide, the blue ferric complex cannot be made directly from a ferric salt, but must be prepared by oxidation of the red ferrous complex II. When ferric chloride solution, for instance, is treated with orthophenanthroline, gradual hydrolysis occurs and finally ferric hydroxide and the soluble hydrochloride of the base are formed. As a result, below a pH of about 3, ferric ions and orthophenanthroline do not react and if the base is added to an equimolecular acid mixture of ferric and ferrous ions in contact with an inert electrode, the potential change may be attributed wholly to the change in concentration of ferrous ion.

The potential developed at an inert electrode in an equimolecular concentration of ferric and ferrous ions is given by the equation

$$E_1 = E_0 + \frac{RT}{nF} \text{ Ln } \frac{a^1_{Fe^{+++}}}{a^1_{Fe^{++}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

using the Faraday Chemical Society terminology. Addition of orthophenanthroline now leads to complex formation with the ferrous ion only, causing a

diminution in activity to the value $a^{11}_{Fe}{++}$. The new potential of the system, E_2, is given by

$$E_2 = E_0 + \frac{RT}{nF} \text{ Ln } \frac{a^{1}_{Fe}{+++}}{a^{11}_{Fe}{++}} \qquad (2)$$

Combining (1) and (2),

$$E_2 - E_1 = \frac{RT}{nF} \text{ Ln } \frac{a^{1}_{Fe}{++}}{a^{11}_{Fe}{++}}$$

i.e.,

$$\frac{a^{1}_{Fe}{++}}{a^{11}_{Fe}{++}} = 10^{\frac{E_2 - E_1}{0 \cdot 059}} \text{ at } 25^\circ \text{ C.}$$

or using concentrations instead of activities in view of the dilution employed and the accuracy attainable in the measurements

$$\frac{c^{1}_{Fe}{++}}{c^{11}_{Fe}{++}} = 10^{\frac{\Delta E}{0 \cdot 059}} \qquad (3)$$

Then in the expression for the instability constant:

$$K_1 = \frac{c_{Fe}{++} \times c^3_B}{c_{(FeB3)}{++}} \qquad (4)$$

where B represents orthophenanthroline, since the dissociation of the complex is extremely small, the final concentration of the tris-orthophenanthroline ferrous ion may be assumed to be equal to the initial total concentration of ferrous ion.

Hence the term

$$\frac{C_{Fe}{++}}{c_{(FeB3)}{++}} = \frac{c^{11}_{Fe}{++}}{c^{1}_{Fe}{++}} = 10^{-\frac{\Delta E}{0 \cdot 059}} \qquad (5)$$

or

$$K_1 = 10^{-\frac{\Delta E}{0 \cdot 059}} \times c^3_B \qquad (6)$$

In order to determine the concentration of free orthophananthroline base in an acid solution of pH=2 containing excess acid, in which the base is present predominantly as the salt, it is necessary to know the hydrolysis constant of the orthophenanthrolinium ion B^+.

The relevant equation for hydrolysis is:

$$BH^+ + (H_2O) \rightleftarrows B + H^+ + (H_2O)$$

whence $K_H = \frac{c_B \times c_{H^+}}{c_{BH^+}}$.

The value of K_H may be determined readily by mixing known weights of the free base and the salt in aqueous solution and measuring the pH, provided the assumption is made that the relative amounts of free base and salt do not alter appreciably in solution. This assumption is reasonable since the degree of hydrolysis of the salt is only of the order of 1%.

K_H was found to be $10^{-5 \cdot 2}$.

Substituting in (6),

$$K^1 = 10^{-\frac{\Delta E}{0 \cdot 059}} \times \left(\frac{K_H \times c_{BH^+}}{c_{H^+}}\right)^3$$

$$= 10^{-\frac{\Delta E}{0 \cdot 059}} \times 10^{-15 \cdot 6} \times \frac{c^3_{BH^+}}{c^3_{H^+}}$$

In all of the above calculations orthophenanthroline has been assumed to be a monoacid base. The authors have shown by potentiometric titration that only one of the nitrogen atoms reacts basically in these experiments.

EXPERIMENTAL.

Ferrous sulphate A.R. containing less than 0·01% of ferric sulphate was used to prepare an M/50 solution which was made up with oxygen-free water and sulphuric acid to an acid concentration of 0·01 N. The ferric salt solution was prepared by oxidation of A.R. ferrous sulphate with chlorine gas which was subsequently boiled out. The final solution was M/50 with respect to ferric ions and 0·1 N with respect to sulphuric acid.

Orthophenanthroline was prepared by the Skraup method from 8 aminoquinoline (Richter and Smith, 1944). The substance was distilled under vacuum and finally recrystallized several times from water. The white needles of the monohydrate melted at 99° C.

Procedure.

(I) The Hydrolysis Constant of Orthophenanthroline.

Orthophenanthroline (0·5 g.) was dissolved in 10 ml. of 0·1002 N hydrochloric acid and the solution diluted to 100 ml. The pH as measured by a glass electrode was found to be 5·35, the same figure being obtained in three experiments. The marked acidity of the solution results from hydrolysis of the orthophenanthroline hydrochloride since theoretically the ratio of base to acid is greater than 1 (here 2·5 : 1).

Then substituting in the expression, $K_H = \frac{c_B \times c_{H^+}}{c_{BH^+}}$, the hydrolysis constant was found to be $10^{-5 \cdot 2}$.

From the hydrolysis constant the dissociation constant may also be estimated. Taking K_w as 10^{-14} at 25° C., it follows that the dissociation constant for orthophenanthroline (K_b) is $10^{-8 \cdot 8}$ or $pK_b = 8 \cdot 8$. The complementary pK_a value is 5·2. Albert and Goldacre (1945) have reported the value 4·8 for pK_a; this value was obtained from pH measurements using a glass electrode on solutions of orthophenanthroline in 50% ethanol, the value in water being obtained approximately by applying Mizutani's correction (Albert, 1945).

(II) Measurement of the Redox Potential.

Ten ml. each of the M/50 ferrous and ferric salt solutions and sulphuric acid 0·1 N were placed in a glass electrode titration flask carrying a saturated calomel half cell and a platinum foil redox electrode. The pH of the system was first measured with a glass electrode and then the redox potential. A known weight of solid orthophenanthroline monohydrate was then added, this weight being in excess of that required to form the ferrous complex but not enough to raise the pH to the precipitation point for ferric hydroxide. The mixture was then shaken thoroughly until the base had dissolved completely. The pH and redox potential were then determined frequently until equilibrium was attained. The final equilibrium was reached in about one hour, and did not change even when the system was left overnight. The details of pH and redox potentials are shown in Table I.

As the mean of four experiments, the value of $K_I = 10^{-17 \cdot 1 \pm 0 \cdot 8}$ was obtained.

TABLE I.

Expt. No.	Initial pH.	Initial Redox Potential.	Weight o-phen. (g.)	Final pH.	Final Redox Potential.	ΔE	Excess Milli-moles Ortho-phenanth.	Concn. BH^+.	K_1.
1	1·45	0·500	0·595	2·03	0·726	0·226	3·00	0·080	$10^{-16 \cdot 5}$
2	1·38	0·494	0·1983	1·55	0·657	0·163	1·00	0·00133	$10^{-18 \cdot 7}$
3	1·32	0·494	0·3966	1·60	0·700	0·206	2·01	0·047	$10^{-18 \cdot 3}$
4	1·20	0·487	0·500	1·46	0·700	0·213	2·53	0·623	$10^{-17 \cdot 3}$

(III) The Estimated Instability Constant for the Ferrous tris-2 : 2′ Dipyridyl Ion.

The structure of 2 : 2′ dipyridyl (IV) and orthophenanthroline are similar, as are the structures and colours of the ferrous and ferric complexes. Further, the ferric complex cannot be made directly by reaction between the free base and a ferric salt. It is thus possible to estimate the instability constant of the ferrous complex by the same method as used with orthophenanthroline. However, insufficient material was available to make the determination directly, but if the assumption is made that the hydrolysis constant of 2 : 2′ dipyridyl is similar to that of orthophenanthroline, an approximate estimate can be made. The redox potential of the ferrous 2 : 2′ dipyridyl complex has been found to be 0·97 volt (Hume and Kolthoff, 1943), as against 1·06 for the phenanthroline complex, i.e. a decrease of 0·09 volt. The decrease can be attributed to the greater dissociation of the 2 : 2′ dipyridyl complex and hence by subtracting 0·09 volt from $\triangle E$ in each experiment with orthophenanthroline and recalculating, an approximate value for the instability constant of the tris 2 : 2′ dipyridyl ferrous ion can be found. This value is found to be 10^{-15}.

Summary.

The instability constant for the tris orthophenanthroline ferrous ion has been found to be $10^{-17 \cdot 1 \pm 0 \cdot 8}$ as a mean of four determinations, by an oxidation reduction potential method. From the known redox potentials of the tris orthophenanthroline and tris 2 : 2′ dipyridyl ferrous ions the instability constant of the tris 2 : 2′ dipyridyl ferrous ion is estimated to be 10^{-15}.

Acknowledgement.

The authors are indebted to Dr. A. Albert for samples of orthophenanthroline, 2 : 2′ dipyridyl and 8 nitroquinoline.

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DERIVATIVES OF 2 : 3-DIPHENYL INDOLE.

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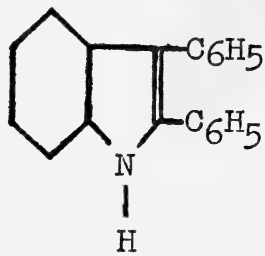
In 1894 Japp and Murray found that when benzoin was heated with a mixture of aniline and aniline hydrochloride, it was converted to 2 : 3-diphenyl-indole (I*a*). Similarly *o*- and *p*-toluidines and α- and β-naphthylamines gave the corresponding indole derivatives in yields approximating 75%. The reaction was extended to secondary aromatic amines by Richards (1910) but the yields obtained were not stated. Little attention was devoted to this reaction until Plant and Tomlinson (1933) in the course of work on substitution in indole derivatives, examined the bromination of 1-acetyl-2 : 3-diphenyl-indole (II*a*). This substance, which they obtained from diphenyl-indole by the action of acetyl chloride in the presence of alkali (yield not stated), was shown to be converted to either the 4- or 6-bromo derivative. Koelsch (1944) proved that the product was the latter by converting it to the known 3-bromo-fluorenone as follows. Diphenyl-indole, obtained in 87% yield by boiling a mixture of benzoin, aniline and hydrochloric acid, was acetylated by refluxing with acetic anhydride and potassium acetate in 71% yield. When the bromination product of this substance was oxidized by chromic anhydride in acetic acid it afforded 2-(N-acetyl-N-benzoylamino)-4-bromo-benzophenone in 55% yield, in turn hydrolysed by 50% sulphuric acid to 2-amino-4-bromo-benzophenone (55% yield). Diazotization of this, followed by warming, gave 3-bromo-fluorenone. The series of reactions, condensation with benzoin to a diphenyl indole, acetylation, oxidation, hydrolysis and diazotization, thus appeared to be a promising method for converting primary aromatic amines to derivatives of fluorene. This paper reports a study of the application of these reactions to the toluidines and certain xylidines.

Under the conditions used by Koelsch, benzoin reacted with *o*- and *p*-toluidines to form 7-methyl (I*b*) and 5-methyl-2 : 3-diphenyl-indoles (I*c*) respectively, in about 90% yield. Depending upon the position of ring closure *m*-toluidine could yield either (or both) the 4- or 6-methyl isomer. Actually only one substance was formed, and this was later shown to be *6-methyl-2 : 3-diphenyl-indole** (I*d*), by converting it to 3-methyl-fluorene. 2 : 3-, 2 : 4- and 2 : 5-dimethyl-anilines afforded *6 : 7-* (I*e*), *5 : 7-* (I*f*) and *4 : 7-dimethyl-2 : 3-diphenyl-indoles* (I*g*) respectively in equally high yields, but N-methyl and N-ethyl-anilines gave the corresponding N-alkyl derivatives in only 50% yields. When iodine was used instead of hydrochloric acid as the catalyst in these reactions, the yields were nearly halved and the crude products were difficult to purify. However, *p*-toluene-sulphonic acid was as effective as hydrochloric acid, and being non-volatile, it may prove more useful with very weakly basic amines (see Richards, *loc. cit.*).

When diphenyl-indole was used, the acetylation procedure of Plant and Tomlinson was found to be inferior to that of Koelsch and so after a few experiments the former method was abandoned. The *N-acetyl-derivatives* II*c* and II*d* were readily obtained from I*c* and I*d*, but the reaction failed with I*b*, I*e*, I*f* and I*g*, the substances being recovered unchanged excepting for some resinification.

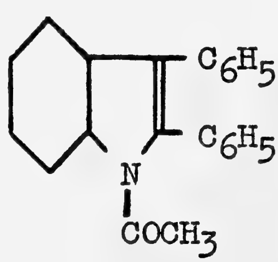
* Substances described for the first time are printed in italics in the theoretical section.

The failure of the reaction is probably due to steric hindrance of the nitrogen atom. Since somewhat similarly constituted carbazole derivatives can be easily acetylated by acetic anhydride with zinc chloride as catalyst (Kehrman, Oulevay and Regis, 1913), this method was applied. Many trials were carried out to determine the best conditions, but even then the procedure finally evolved gave low yields. The reaction was a complex one. The purification of the products



Ia			
Ib	7-CH_3	Ie	6:7-$(CH_3)_2$
Ic	5-CH_3	If	5:7-$(CH_3)_2$
Id	6-CH_3	Ig	4:7-$(CH_3)_2$

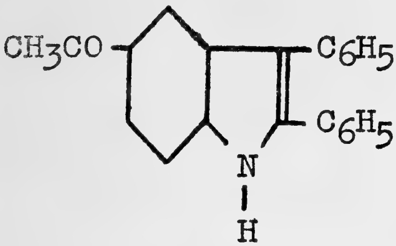
was rendered tedious by the formation of tar and amorphous materials, and it is by no means certain that all of the products from each indole were isolated N-methyl and N-ethyl-diphenyl-indoles gave only tars, but diphenyl-indole formed a purple *substance* of undetermined constitution. I*c* yielded the N-acetyl derivative (II*c*) plus an isomeric *ketone* and similar results were obtained with I*f* and I*g*. However, I*e* gave only the *N-acetyl derivative* II*e*, and I*b* and I*d* only *ketones*.



IIa		IIe	6:7-$(CH_3)_2$
IIc	5-CH_3	IIf	5:7-$(CH_3)_2$
IId	6-CH_3	IIg	4:7-$(CH_3)_2$

With one exception the ketones could be distinguished from the N-acetyl derivatives by the formation of dinitro-phenylhydrazones. Since Borsche and Groth (1941) have shown that indoles are acetylated in the 5 position in the

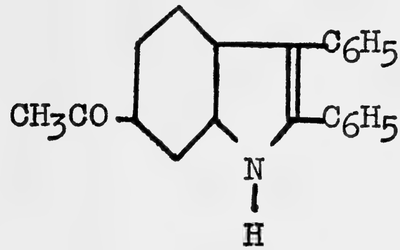
Friedel-Crafts reaction, the ketones from I*b*, I*d* and I*g* are probably III*b*, III*d* and III*g* respectively. When the 5 position is already



IIIb 7-CH_3

IIId 6-CH_3

IIIg 4:7-$(CH_3)_2$



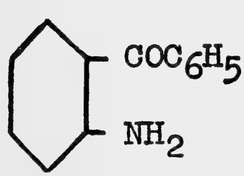
IIIc 5-CH_3

IIIf 5:7-$(CH_3)_2$

occupied as in I*c* and I*f*, it is considered probable that the ketones are III*c* and III*f*, respectively (see Plant and Tomlinson, *loc. cit.*). Neither of the substances obtained from I*f* reacted with dinitrophenylhydrazine and so a distinction by this means was not possible, since III*f* would be unlikely to react because of steric hindrance. However, since neither of them could be converted to a benzophenone derivative, the matter was not pursued.

By a slight modification of Koelsch's oxidation procedure, nearly quantitative yields were obtained. No attempt was made to isolate the products in the pure state, since preliminary experiments showed that the yield of 2-aminobenzophenone from the hydrolysis of crude 2-(N-acetyl-N-benzoylamino)-benzophenone was as high as the yield obtained from the pure substance. It was also found that acetylation of the indoles before oxidation was essential.

The hydrolysis was studied under a large variety of conditions, but no procedure better than Koelsch's was discovered. By this method 5-methyl-(IV*c*), 4-*methyl-*(IV*d*) and *3 : 4-dimethyl-2-amino-benzophenones* (IV*e*) were readily prepared, but surprisingly the other oxidation products yielded no

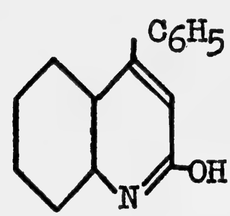


IVa

IVc 5-CH_3

IVd 4-CH_3

IVe 3:4-$(CH_3)_2$



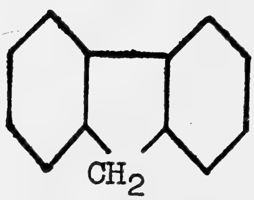
Va

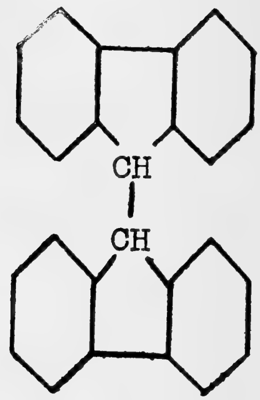
Vc 6-CH_3

Vd 7-CH_3

crystalline substances. When alcoholic potassium hydroxide was used to hydrolyse the oxidation products of II*a*, II*c* and II*d*, there was produced together with the expected aminobenzophenones, 4-phenyl-carbostyril (V*a*), its *6-methyl* (V*c*) and *7-methyl* (V*d*) derivatives respectively. The constitution of these substances follows from the observation by Camps (1899) that 2-acetylamino-benzophenone is cyclized by dilute alkali to 4-phenyl-carbostyril.

Diazotization of IV*c*, IV*d* and IV*e* followed by warming (Graebe and Ullmann, 1896) produced 2-methyl-, 3-methyl, and *3 : 4-dimethyl-fluorenones* respectively, together with small amounts of the corresponding hydroxyketones. There are few references in the literature to the Clemmensen reduction of fluorenones. Miller and Bachman (1935) claim to have reduced 2-, 3- and 4-bromo-fluorenones to the bromofluorenes in nearly quantitative yield. But it was found that fluorenone gave not only fluorene (VI*a*) but also 9 : 9′-di-fluorenyl (VII*a*), even when the fluorenone was added slowly to a large excess of





VIa		VIIa	
VIc	2-CH_3	VIIc	2:2′-$(CH_3)_2$
VId	3-CH_3	VIId	3:3′-$(CH_3)_2$
VIe	3:4-$(CH_3)_2$	VIIe	3:3′:4:4′-$(CH_3)_4$

zinc filings. This substance, identified by direct comparison with an authentic specimen (Graebe and Stindt, 1896) was easily separated from fluorene because of its low solubility and low volatility. In a similar way 2-methyl-fluorene (VI*c*) and *2 : 2′-dimethyl-9 : 9′-difluorenyl* (VII*c*), 3-methyl-fluorene (VI*d*) and *3 : 3′-dimethyl-9 :,9′-difluorenyl* (VII*d*), *3 : 4-dimethyl-fluorene* (VI*e*) and *3 : 3′ : 4 : 4′-tetramethyl-9 : 9′-difluorenyl* (VII*e*) were obtained. Such binuclear hydrocarbons do not appear to have been previously recorded as products in Clemmensen reductions (Martin, 1942).

The study of these reactions and of the by-products will be continued.

Experimental.

In the following, only the general procedures as finally developed are described.

Indole Synthesis.

A mixture of benzoin (50 g.), the aromatic amine (100 g.) and concentrated hydrochloric acid (12 c.c.) was boiled in a flask fitted with a short air condenser for one hour. Heating was

regulated so that the minimum of amine escaped from the top of the condenser. After cooling, the reaction mixture was shaken with ether and dilute acid. The ether extract after another washing with acid was washed with alkali, dried, charcoal and evaporated. The crude product remaining was then recrystallized from an appropriate solvent. Unreacted amine was easily recovered from the acid washings. With iodine (12 g.) as catalyst the yields were about half of those listed below, but *p*-toluene-sulphonic acid (20 g.) was as efficient as hydrochloric acid.

2 : 3-Diphenyl-indole (*Ia*), obtained in 88% yield crystallized from 90% methanol in colourless needles, m.p. 124° C.

1-Methyl-2 : 3-diphenyl-indole, 52% yield, from 1 : 1 alcohol-ethyl acetate, colourless needles m.p. 136° C.

1-Ethyl-2 : 3-diphenyl-indole, 50% yield, from 1 : 1 alcohol-ethyl acetate, rectangular plates, m.p. 133° C.

7-Methyl-2 : 3-diphenyl-indole (*Ib*), 92% yield, from 90% methanol, colourless tablets, m.p, 128° C.

5-Methyl-2 : 3-diphenyl indole (*Ic*), 93% yield, from methanol plus a little acetone, colourless needles, m.p. 153° C.

6-Methyl-2 : 3-diphenyl-indole (*Id*). The crude product was converted to its picrate in alcohol and the picrate fractionally crystallized from this solvent. All fractions were homogeneous and identical. The regenerated substance crystallized from 90% methanol in colourless prisms, m.p. 118° C.

Found : C, 88·2 ; H, 5·9%. Calculated for $C_{21}H_{17}N$: C, 89·0 ; H, 6·0%.

The *picrate* formed deep reddish brown needles, m.p. 166° C.

Found : N, 10·9%. Calculated for $C_{27}H_{20}O_7N_4$: N, 10·9%.

6 : 7-Dimethyl-2 : 3-diphenyl-indole (*Ie*), 90% yield, from alcohol, colourless rhombs, m.p. 144° C.

Found : C, 88·9 ; H, 6·5%. Calculated for $C_{22}H_{19}N$: C, 88·9 ; H, 6·4%.

The *picrate* formed small dark brown needles from alcohol m.p. 162°–163° C.

Found : N, 10·6%. Calculated for $C_{28}H_{22}O_7N_4$: N, 10·6%.

5 : 7-Dimethyl-2 : 3-diphenyl-indole (*If*), 92% yield, from alcohol, colourless prisms, m.p. 149°C

Found : C, 88·4 ; H, 6·5%. Calculated for $C_{22}H_{19}N$: C, 88·9 ; H, 6·4%.

The *picrate* crystallized from alcohol in dark brown needles m.p. 157°–158° C.

Found : N, 10·6%. Calculated for $C_{28}H_{22}O_7N_4$: N, 10·6%.

4 : 7-Dimethyl-2 : 3-diphenyl-indole (*Ig*), 89% yield, from 90% methanol in irregular colourless plates, m.p. 130° C.

Found : C, 88·4 ; H, 6·5%. Calculated for $C_{22}H_{19}N$: C, 88·9 ; H, 6·4%.

The *picrate* separated from alcohol in deep reddish brown needles, m.p. 132° C.

Found : N, 10·6%. Calculated for $C_{28}H_{22}O_7N_4$: N, 10·6%.

Acetylation of the Indoles.

(*1*) *With acetic anhydride and potassium acetate.* The procedure of Koelsch was followed.

1-Acetyl-5-methyl-2 : 3-diphenyl-indole (*IIc*), obtained in 75% yield, crystallized from glacial acetic acid in colourless needles, m.p. 176° C.

Found : C, 84·9 ; H, 5·9%. Calculated for $C_{23}H_{19}ON$: C, 84·9 ; H, 5·9%.

1-Acetyl-6-methyl-2 : 3-diphenyl-indole (*IId*), produced in 67% yield, separated from alcohol in irregular crystals with marked twinning, m.p. 127° C.

Found : C, 84·7 ; H, 5·9%. Calculated for $C_{23}H_{19}ON$: C, 84·9 ; H, 5·9%.

(*2*) *With acetic anhydride and zinc chloride.* The indole (10 g.) was dissolved or suspended in acetic anhydride (50 c.c.) and treated with powdered anhydrous zinc chloride (1 g.) at room temperature. The mixture was stirred for one hour and then heated to 70°–75° C. for fifteen minutes. After dilution with water the dark product was collected, washed and dried. The details of purification are recorded below, under the headings of the individual indole numbers.

(*1a*) The product was washed thoroughly with warm alcohol and then crystallized several times from glacial acetic acid. It (3 g.) formed small purple leaflets, m.p. 256° C. It was sparingly soluble in the usual solvents.

Found: C, 84·4; H, 5·5; N, 4·6%. Calculated for $(C_{22}H_{17}ON)_n$: C, 84·9; H, 5·5; N, 4·5%.

No other crystalline substance could be isolated from the alcoholic washings.

(*1b*) The black solid was boiled with alcohol (75 c.c.), cooled and collected. Repetition of this treatment gave a light coloured residue, which was crystallized from ethyl acetate with the aid of charcoal. *5-Acetyl-7-methyl-2 : 3-diphenyl-indole* (*IIIb*) formed colourless needles (3·9 g.), m.p. 235° C. It gave a positive test with dinitrophenyl-hydrazine.

Found: C, 85·3; H, 5·9; N, 4·3%. Calculated for $C_{23}H_{19}ON$: C, 84·9; H, 5·9; N, 4·3%.

Only amorphous materials could be obtained from the alcoholic washings.

(*1c*) The product was extracted twice with boiling alcohol (2× 100 c.c.). The residue, after crystallization from acetic acid, gave pure *IIc* (2·3 g.). The alcoholic filtrates after concentrating to half bulk and cooling deposited a substance which after many recrystallizations from alcohol-ethyl acetate was finally obtained pure (1·7 g.). *6-Acetyl-5-methyl-2 : 3-diphenyl-indole* (*IIIc*) formed colourless needles m.p. 161° C., and gave a positive test with dinitrophenylhydrazine.

Found: N, 4·2%. Calculated for $C_{23}H_{19}ON$: N, 4·3%.

(*1d*) Crystallization from benzene and then alcohol afforded *5-acetyl-6-methyl-2 : 3-diphenyl-indole* (*IIId*) as pale yellow needles m.p. 187° C. (4·1 g.), which gave a positive test with dinitrophenylhydrazine.

Found: N, 4·2%. Calculated for $C_{23}H_{19}ON$: N, 4·3%.

The solid residue obtained by evaporating the filtrates could not be separated into its constituents.

(*1e*) The residue obtained by washing thoroughly with warm alcohol was crystallized from ethyl acetate to yield *1-acetyl-6 : 7-dimethyl-2 : 3-diphenyl-indole* (*IIe*) as colourless prisms (4·4 g.) which melted at 222° C. Excepting an additional amount of this substance (0·3 g.) no pure substance could be isolated from the alcoholic filtrates.

Found: C, 84·7; H, 6·2%. Calculated for $C_{24}H_{21}ON$: C, 85·0; H, 6·2%.

(*1f*) The product was crystallized firstly from alcohol-ethyl acetate to remove dark impurities, and then fractionally crystallized from acetone and acetone-alcohol. The less soluble *substance* crystallized from acetic acid in colourless prismatic needles (1 g.) melting at 238° C. (*IIf* or *IIIf*).

Found: C, 84·5; H, 6·3; N, 4·1%. Calculated for $C_{24}H_{21}ON$: C, 85·0; H, 6·2; N, 4·1%.

The more soluble *substance* (2·3 g.) formed colourless hairs m.p. 191° C., from alcohol-ethyl acetate (*IIIf* or *IIf*).

Found: C, 84·4; H, 6·2; N, 4·1%. Calculated for $C_{24}H_{21}ON$: C, 85·0; H, 6·2; N, 4·1%.

Neither of these substances reacted with dinitrophenylhydrazine.

(*1g*) After washing twice by stirring with warm alcohol (2× 50 c.c.) the residue was crystallized twice from alcohol and then from benzene, forming colourless blades (2·8 g.). *1-Acetyl-4 : 7-dimethyl-2 : 3-diphenyl-indole* (*IIg*) melted at 204° C.

Found: C, 84·8; H, 6·4%. Calculated for $C_{24}H_{21}ON$: C, 85·0; H, 6·2%.

The combined dark green alcoholic filtrates were evaporated to a small bulk (about 25 c.c.) and then cooled. The material which separated, after washing with alcohol and crystallizing many times from methanol with aid of charcoal, finally afforded *5-acetyl-4 : 7-dimethyl-2 : 3-diphenyl-indole* (*IIIg*) as pale yellow needles (0·6 g.), melting at 224° C.

Found: C, 84·6; H, 6·0; N, 4·3%. Calculated for $C_{24}H_{21}ON$: C, 85·0; H, 6·2; N, 4·1%.

This substance gave a positive test with dinitrophenylhydrazine.

Oxidation of N-Acyl Derivatives.

A stirred suspension of the indole derivative (10 g., 3 mol.) in glacial acetic acid (100 c.c.) was treated at room temperature with a solution of chromic anhydride (4 mol.) in a little water. After stirring for two hours at this temperature the mixture was heated on the water bath for thirty minutes, then diluted and extracted with ether. The extract, after washing with dilute sodium carbonate solution, yielded the crude product on evaporation.

Hydrolysis.

(*1*) *With sulphuric acid.* A mixture of the oxidation product (10 g.), concentrated sulphuric acid (50 c.c.) and water (50 c.c.) was refluxed for three hours, then cooled, diluted and poured into excess dilute ammonia. The dark ether extract of this, after filtration, was evaporated and the residue extracted with boiling dilute hydrochloric acid (100 c.c. of 3 N). After charcoaling, the acid extract was basified with ammonia and the product collected. Purification was best effected by crystallization from light petroleum.

2-Amino-benzophenone (IV*a*) was obtained in 68% overall yield from II*a*.

5-Methyl-2-amino-benzophenone (IV*c*) in 71% yield, crystallized in pale yellow needles, m.p. 63° C. Chattaway and Lewis (1904) give m.p. 60° C.

4-Methyl-2-amino-benzophenone (IV*d*) in 67% yield, formed long yellow needles, m.p. 66° C. Found: C, 79·0; H, 6·2%. Calculated for $C_{14}H_{13}ON$: C, 79·6; H, 6·2%.

3 : 4-Dimethyl-2-amino-benzophenone (IV*e*) in 61% yield, crystallized in yellow plates, m.p. 103° C.
Found: C, 79·8; H, 6·7%. Calculated for $C_{15}H_{15}ON$: C, 80·0; H, 6·7%.

(*2*) *With alcoholic potassium hydroxide.* A solution of the oxidation product (10 g.) and potassium hydroxide (25 g.) in alcohol (100 c.c.) was refluxed for three hours and then evaporated to dryness. The residue was nearly neutralized with dilute acetic acid and then collected. By extraction with hot dilute hydrochloric acid, the amino ketone was readily separated from the quinoline derivative.

II*a* gave IV*a* (2·8 g.) and *4-phenyl-carbostyril* (V*a*) (1·8 g.) melting at 256° C. (Camps, *loc. cit.*).

II*c* gave IV*c* (2·3 g.) and *6-methyl-4-phenyl-carbostyril* (V*c*) (1·7 g.) crystallizing from alcohol in long colourless fluffy needles, m.p. 238° C.
Found: N, 5·9%. Calculated for $C_{16}H_{13}ON$: N, 6·0%.

II*d* gave IV*d* (2·5 g.) and *7-methyl-4-phenyl-carbostryil* (V*d*) (1·8 g.) forming colourless needles, m.p. 281° C. from alcohol.
Found: N, 6·0%. Calculated for $C_{16}H_{13}ON$: N, 6·0%.

Fluorene Synthesis.

A solution of the amino ketone (10 g.) in concentrated sulphuric acid (25 c.c.) and water (125 c.c.) was diazotised as usual and then heated on the water bath until nitrogen was no longer evolved. After cooling, the product was extracted with ether and the hydroxy ketone removed by three extractions with 15% potassium hydroxide solution. Evaporation of the ether left the crude fluorenone derivative, purified by crystallization from light petroleum, and acidification of the combined alkali extracts yielded the hydroxy ketone.

From IV*c* there was obtained *2-methyl-fluorenone* (6 g.), long yellow needles, m.p. 92° C. in agreement with Kruber (1932) and *2-hydroxy-5-methyl-benzophenone* (2·6 g.), pale yellow leaflets, m.p. 84° C. from aqueous alcohol (lit. 84° C.).

IV*d* gave *3-methyl-fluorenone* (7·3 g.) yellow prismatic needles, m.p. 68° C. (Kruber, *loc. cit.*, gives 69° C.) and *2-hydroxy-4-methyl-benzophenone* (1·8 g.), pale yellow irregular plates from aqueous methanol m.p. 60° C. (lit. 60° C.).

IV*e* yielded *3 : 4-dimethyl-fluorenone* (9·1 g.), yellow needles, m.p. 117° C.
Found: C, 86·0; H, 5·8%. Calculated for $C_{15}H_{12}O$: C, 86·5; H, 5·8%.
Only traces of hydroxy ketone were formed.

Clemmensen Reduction.

A solution of the fluorenone (3 g.) in hot alcohol (40 c.c.) was added during three hours to a boiling mixture of amalgamated zinc filings (50 g.), water (10 c.c.) and concentrated hydrochloric acid (25 c.c.). During this period more acid (25 c.c.) was also added and a further amount (30 c.c.) through the next three hours. After cooling, the mixture was extracted thoroughly with a large volume of ether, which after washing and drying, was evaporated. The residue was boiled with alcohol (130 c.c.) and then cooled. The insoluble portion was the crude difluorenyl. The fluorene was isolated from the alcoholic solution by taking it to dryness and then evaporating the residue on to a cold finger under reduced pressure.

Fluorenone gave VI*a* (1·9 g.) and VII*a* (0·4 g.), colourless needles, m.p. 241° C. from benzene (lit. 246° C. corr.).

2-Methyl-fluorenone gave VIc (1·7 g.), colourless leaflets from alcohol, m.p. 104° C. (Kruber, *loc. cit.*) and VIIc (0·6 g.), colourless needles from benzene, m.p. 258° C.

Found: C, 93·8; H, 6·0%. Calculated for $C_{28}H_{22}$: C, 93·9; H, 6·1%.

3-Methyl-fluorenone gave VI*d* (1·7 g.), colourless irregular plates from alcohol, m.p. 89° C. (Sieglitz and Schatzkes, 1921, give 88° C.), and VII*d* (0·5 g.), colourless needles from acetic acid, m.p. 236° C.

Found: C, 93·7; H, 6·1%. Calculated for $C_{28}H_{22}$: C, 93·9; H, 6·1%.

3:4-Dimethyl-fluorenone afforded VI*e* (1·4 g.) colourless irregular plates, m.p. 100° C. from alcohol.

Found: C, 92·3; H, 7·1%. Calculated for $C_{15}H_{14}$: C, 92·8; H, 7·2%.

VII*e* (1·1 g.) formed at the same time, crystallized from acetic acid in colourless needles, m.p. 264° C.

Found: C, 92·9; H, 6·7%. Calculated for $C_{30}H_{26}$: C, 93·3; H, 6·7%.

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THE PULSE OF THE PACIFIC.*

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"There needs a long time to know the earth's pulse."
—From selections by George Herbert, published 1639.

The author of this old English proverb spoke better than he knew, for the science of Geology was still unborn.

Through the earliest mists of geological time the rhythmic rise and fall of the ocean can be discerned. The throb of its pulse beating against its bounds has been felt through all the ages.

The wave-sculptured shores bear records revealing those multitudinous oscillations of the strand which have had such a pregnant influence on the face of the earth, and on the life of its inhabitants.

The longer rhythms of time are marked by the eras and periods now recognised by geologists. Within the larger periods are shorter rhythms, marked by the frequent coming and going of the seas. Though the impress of their impact grows fainter with age, and may even vanish, there are many features of the younger seas which can still be clearly seen. It is for this reason that in this study attention is directed to the nature and causes of strand line changes in late geological time.

The whole ocean surface has shared in such movements, and the problem of strand line changes is one of world-wide scope.

The Pacific Ocean has been chosen for study partly because it forms one great unit, and in particular because it washes Australian shores.

An examination of present-day shore lines reveals striking diversities in their appearance and character. These are in part due to variations in the resistance of the rocks to the attack of the sea, and in part to the structure of the rock masses.

The resistance to erosion may sometimes be slight. This is illustrated by the history of Graham Island, which was built up from the floor of the Mediterranean Sea between Sicily and Africa by a submarine eruption in 1831. The material ejected was fragmental, and the island was built of volcanic ash which had little more resistance than sand. Although the island was originally 200 feet high it was completely demolished by the waves of the comparatively quiet Mediterranean Sea in the course of three months. Only a shoal now marks its place.

On the other hand islands built by hard lavas may endure for many millions of years.

Rocks of sedimentary origin such as sandstones and shales vary greatly in their resistance, the shales as a rule being more rapidly cut away than the sandstones. To such differences are due the fine beaches and rugged headlands of sandstone in the Sydney district.

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* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, June 20, 1946.

The resistant headlands of a coast are characteristically cut back to cliff faces, the bases of which are undercut to form a notch extending a little above sea-level. Rock platforms gently sloping seawards are also commonly developed.

In the beach zone the storm waves may build up a storm beach above the high tide level, and the windswept beach sands may be swept up into sand dunes behind the active beach. In the beach zone and below it sea shells live and die, and their remains may be preserved under the beach sands.

These are some of the chief shore-line features which may be preserved along a coast from which the sea has recently receded ; and their presence above the present sea-level constitutes proof of a former higher stand of the sea. Other features will be considered later when such evidence around the borders of the Pacific Ocean is being considered.

Evidences of rises in sea level are less abundant, as the sea itself covers, and may obliterate, the preceding shore-line features. The presence of level submarine shelves and of shallow water fossils at depths, in positions remote from the present shore line, point to submergence. The beds of rivers which are continued for some miles from the coast as channels in the floor of the sea also favour submergence.

A study of the literature dealing with coastal features around the margin of the Pacific Ocean, and of the islands within its bounds, shows that strand line changes have been numerous in Pleistocene and Recent time. A general survey of these will now be given, commencing with the South-west Pacific, and proceeding round the margin of the Pacific *via* Japan and Alaska to the eastern borders of this great ocean. Island arcs within the Pacific will also be considered.

Strand Line Changes in the Pacific Ocean.

The Australian Region.

At the meeting of the Pan-Pacific Science Congress in Japan in 1926 I presented a short statement (Cotton, 1926) of strand-line movements in Australia in Pleistocene and post-Pleistocene time. This formed part of a discussion on this subject which I had previously recommended for consideration at this conference. Interest in this subject has been maintained at subsequent meetings and a considerable amount of information is now available.

The problem of strand line changes in Australia is of special interest in relation to the advent of aboriginal man, first into northern Australia, and later into Tasmania. It is considered that the primitive man of Pleistocene time had no means of crossing wide stretches of water, and hence he must have arrived along a land-route. Such a route, both to the mainland and Tasmania, might have been open during low stands of sea level a few hundred feet below the present strand.

The evidence for strand line changes in Tasmania has been gathered and discussed by Johnston (1888), Gregory (1903), Loftus Hills (1914), David (1926) and more recently by Lewis (1934).

The confusion of fluvio-glacial terraces with possible marine terraces has been cleared up by David, who recognised only one marine terrace—that at Strahan—where it stands about 15 feet above sea level.

In order to escape this difficulty Lewis carried out investigations in the northern part of the island, which did not undergo glaciation. Here he correlated certain physiographic features with the glacial phases further south and recognised the following strand lines in order of age commencing with the oldest pre-Malanna Stage for which he estimated a strand from 50 to 100 feet above the present level.

During the Malanna Glacial Stage the strand sank to 150 feet below the present level, and rose again during the Malanna-Yolande interglacial epoch to 50 feet above the present strand. With the onset of the Yolande glaciation the strand sank to 60 feet below present sea-level and in the following Yolande-Margaret glacial period rose to 5 to 15 feet above the present strand.

The Margaret glaciation led to a strand 10–25 feet below present sea level, to which it rose again at the close of the Margaret glacial epoch.

This study of Lewis's gives the most complete account of strand line changes yet worked out for an Australian region in connection with the Pleistocene glaciation.

Other physiographic evidence of strand line movements is clear along the eastern coast of Tasmania. At Eaglehawk Neck a coastal lagoon is shut off from the sea by a long sand spit, and this land form is characteristic of a recent sinking of sea level. The magnificent drowned valley of the Derwent estuary and other similar features along the south-eastern coast of Tasmania provide indisputable evidence of a low stand of sea level. The exact amount of this is not yet known, but it appears to have been too great to be explained by a sinking of the land under the load of the Pleistocene ice cap. In any case such a depression would now have been largely compensated by an uplift following the melting of the ice cap, and could not have left as a residual effect the deep submergence of the lower Derwent Valley.

There is need for caution in correlating the Tasmanian strands with those of the mainland. The factor which affects Tasmania and not the mainland is the possible depression of the land under the Pleistocene ice sheets, and the emergence of the land again during the interglacial epochs. The history of strand line movements in Europe and North America has shown that movements of this character amounting to some hundreds of feet have taken place during and following the Pleistocene Ice Age. Residual movements indeed are still in progress in both of these continents. The relatively small size of the Tasmanian ice cap, however, is not likely to have produced large movements of this character.

On the mainland of Australia no such problem arises. Much discussion, however, has taken place with regard to the last movement of the strand for which a sinking of sea level amounting to some 10 to 15 feet has been described.

On the northern shores of Bass Strait and in the vicinity of Melbourne there are, as on the Tasmanian coast, wide shore-platforms which lie between the levels of the high and low tides. These, on the Victorian coast, attain a width in places of from 300 to 600 feet. Beach ridges with marine shells lie at the back of the present-day beaches at an elevation of up to 12 feet.

Jutson (1930), on reviewing the evidence, considers that these features do not give convincing proof of a higher strand level.

Sherbon Hills (1940) recognises a sea-worn bench which varies from 2 to 5 feet above the main rock bench. He also considers that the shell beds near Williamstown represent upraised submarine banks and indicate a former stand of the strand about 8 feet above the present level.

The evidence of the south-eastern coast of South Australia is more clear. Here Tindale (1933) has found a vertical cliff of Tertiary limestone 100 feet in height at the base of which are sea worn caves on the floor of which are shells of marine origin. At the foot of the cliff is a sea-cut terrace standing from 140 to 160 feet above sea level. Between this and the sea is a lower terrace on which lie sand dunes from 20 to 40 feet high. This terrace is a little higher than Tantaloola Railway Station, which is 83 feet above mean sea-level.

A section from Beachport north-easterly to the Naracoorte Range reveals a wonderful succession of sand-ridges which are thought to mark successive stands of the sea. The highest is the oldest and the lower ones are progressively younger.

In descending order of elevation these are :

The Naracoorte Range	.. .. ..	from	250	to 190	feet
The Cave Range	.. ..	,,	200	,, 160	,,
The East Avenue Range	.. .. ..	,,	150	,, 120	,,
The West Avenue Range	.. .. ..	,,	90	,, 80	,,
The Reedy Creek Range	.. .. ..	,,	65	,, 50	,,
The Wookwine Range	.. .. ..	,,	25	,, 10	,,

The marine shells found in the oldest of these sand dunes are of Pleistocene age.

The Marine Fauna. A graphical correlation given with strand lines described by Cooke (1930) from the Atlantic seaboard of U.S.A. shows a marked relationship between the successive strands in these distant coasts, those of U.S.A. standing consistently about 10 feet higher than the corresponding South Australian strands. Clarke (1928) has described a recent raised beach at Port Turton near the eastern entrance to Spencer's Gulf. Here a horizontally bedded beach sand is well compacted and crowded with shells of present day types. This raised beach sands 4 to 5 feet above high water mark, and rests upon limestone of Miocene age. It stands out boldly at the foot of a cliff. This horizon has been found also in pits on the coastal plain adjoining, and is probably of considerable extent. The shells of the raised beach are identical with those living on the beach below.

At many places along the coast of New South Wales there are shore line features giving evidence of a former higher stand of sea level. Harper (1917) has described from the Illawarra district rock platforms standing from 2 to 4 feet above high water mark which in places have a breadth of up to 250 feet. Sea-worn caves were found in a number of places standing at an elevation of about 16 feet above mean sea level.

Coarse shingle and boulder beaches lie at the heads of many small coves at elevations up to 15 feet above mean sea level, and are beyond the reach of storm waves. In addition, there are subdued cliffs standing well back from the present coast with their bases some 15 feet above sea level. Banks of vegetation separate them from the present shore. Coastal lagoons such as Lake Illawarra are separated from the sea by long sandspits extending between headlands. These are characteristic of shores of recent emergence.

Along the coast north of Sydney, rock platforms exposed at low water are conspicuous. At Long Reef the rock platform has a breadth of about 900 feet. Coastal lagoons like those of Lake Illawarra are numerous along this part of the coast, and are characteristic features of the shore for at least 150 miles north of Sydney.

Raised beaches with marine shells identical with species living in the adjacent sea have been described at Largs (David and Etheridge, 1890) and in the Kempsey district (Voisey, 1934). These deposits establish a recent sinking of the strand of from 10 to 15 feet.

Jardine (1925) has described the remnants of a higher sea-cut bench standing on the outer part of the Long Reef platform. This he estimates at 15 feet above the level of the main platform, which itself is 2 to 3 feet below the high water spring tide level. I have found remnants of a similar high level bench on the headlands south of Whale Beach and Palm Beach.

At Bondi a sea-worn cave cut into the base of a decomposed dyke stands about 15 feet above mean sea level.

Hedley (1924) has described a system of three rock benches on the coast between Manly and North Head at Blue Fish Bay. The upper bench stands between 25 and 30 feet above sea level, and has a mazimum width of 25 yards.

The intermediate bench is about 6 feet above the lowest one, and has a width of 40 yards. The lowest bench stands at about half-tide level.

Remnants of river terraces along the Hawkesbury River are well marked at Windsor and Richmond, where they stand about 15 feet above the present flood plain. These were probably graded to the higher stand of the sea at about 12 to 15 feet above its present level.

W. R. Browne (1926) has recorded river terraces in the Hunter River valley which may be related to strand line movements. At about three-quarters of a mile above the Hillborough Bridge terraces were measured standing above the present river level at altitudes of 75, 55 and 35 and 20 feet. The river is here 50 feet above sea level. At Gosforth another set of terraces was found with elevations of 120, 80 and 40 feet above the river level. These are stated to be of Pleistocene and Recent age.

Sussmilch (1940), from a study of the geomorphology of the Lower Hunter Valley, has recognised three terrace levels. These are the Charleston Bench which is 400 to 500 feet above the present river, the East Maitland Bench, from 125 to 130 feet, and the Raymond Terrace Bench, from 15 to 20 feet above the river level. The ages of all these terraces are stated to be Pleistocene to Recent.

Voisey (1934) has recorded for the north coast of New South Wales strand lines at 5, 10, 25, 30, 50, 100 and 200 feet above sea level, and submerged strands at 30, 50 and 70 feet below sea level.

Maze (1945) has made a statistical analysis using altimetric frequency curves for the coastal region of central New South Wales, and concludes that there is evidence for a widespread terrace of from 100 to 150 feet above sea level. He has also found evidences of valley in valley topography concordant with this erosion level, and concludes that his observations point to a former strand line extending up to about 150 feet above present sea level.

There is also evidence for a large depression of sea level. Borings across the Hawkesbury River made in connection with the building of the road bridge reached rock bottom in one place at a depth of 250 feet below sea level. As this occurs some seven miles from the mouth of the river, this evidence points to a sea stand somewhat greater than 250 feet below present sea level.

A still greater submergence is proved by the occurrence of beach remnants found by trawlers between the 70 and 75 fathom contours off the east coast (Hodge Smith and Iredale (1924)). These contain marine shells identical with present-day forms. The faunal assemblage is more related to the forms of the eastern coast of Tasmania than of New South Wales, and this suggests a cooler climate at the time of their deposition.

The study of the Admiralty charts reveals that at the 70 fathom line sand, gravel and stones have been recorded along most of the New South Wales coast.

The shells were found in stone slabs up to 20 square feet in area and 18 inches in thickness. They are similar in character to parts of the present-day beach sands which have been cemented locally by carbonate of lime at the south side of Collaroy beach.

It is important that no coarse deposits have been found inshore from the 70 fathom line.

Iredale states that the shells found have a very shallow water habitat, and the conclusion drawn by both authors is that the deposits represent a sea stand about 400 feet below present sea level.

Minor halting stages in the depressions of sea level may perhaps be indicated by 90 feet submergence of the peat bed at Narrabeen (David and Halligan, 1908) and the 15 feet submergence of the peat bed at Botany Bay (Etheridge, David and Grimshaw, 1896).

Passing northwards along the Queensland coast, erosion effects along the shore diminish in intensity northwards from Rockhampton, owing to the shielding effect of the Great Barrier Reef, which damps down the storm waves of the open Pacific Ocean. In this northern section wave-cut benches are less well developed. Jardine (1925) records that at Mackenzie Island there are marine cliffs and rock benches, distant about 100 yards from the shore, which stand 15 to 20 feet above sea level. These appear to be somewhat higher than similar features on the southern coast of New South Wales.

At Archer Point near Cooktown there is an inconstant development of wave cut benches carved out of strongly folded quartzites and slates. The bench surface slopes seaward from 8 feet to 3 or 4 feet above high water mark There is also an irregular bench cut to about 2 feet below high water level.

At North Keppel Island rock benches occur slightly above high water level, but not beyond storm-wave activity. The rocks consist of horizontally bedded sandstones, quartzites and phyllites of Devonian age.

On Albany Island, Richards and Hedley (1924) have recorded two rock benches, the upper one being 5 to 6 feet above high tide level, and the lower about 2 to 3 feet below high water.

At Black Rocks in Torres Strait dual benching is also present, the levels of the benches approximating to those of high and low water.

At North Barnard Islands between Townsville and Cairns, Hedley (1925) has described a ledge below the lighthouse, which is about 150 yards wide, and stands about 8 feet above mean sea level. There is a notch at the foot of the cliff against which the bench abuts.

From these observations along the Queensland coast there appear to be three systems of rock benches, the highest from 15 to 20 feet, an intermediate bench at about 8 feet, and the lowest bench about mean sea level. The actual stand of the sea depends on the depth at which the rock benches were cut.

At Holbourne Island a phosphatised coral reef 10 feet thick points to a sinking of sea level by at least this amount, as phosphatisation cannot take place below sea level. An early observation by Captain Stokes (1846) on a raised beach some 12 feet above sea level situated at Cape Upstart, 30 miles to the south-west, confirms this sinking of sea level (Marshall, Richards and Walkom, 1925).

The work carried out by the Great Barrier Reef Committee, and the results published by Richards and Hill (1942) has provided important evidence of the history of the strand line in Recent and perhaps late Pleistocene time.

In addition to surface investigations and biological studies of living fauna, the Great Barrier Reef Committee undertook a programme for boring through the coral reef in an attempt to ascertain the foundations of the reef, and, if possible, the depth and character of the basement rock of the continental shelf. While the basement rock was not reached, the foundation on which the coral reef had built was found, and borings continued for some 230 feet below it, yielding important information regarding the depth and age of the strand line movements. Two bores were sunk in the Great Barrier Reef at a distance of about 700 miles apart. The first bore was put down at Michaelmas Cay in latitude 16° 36′ S. This is about 22 miles north-north-east of Cairns. The second bore was sunk at Heron Island in latitude 23° 26′ S., near the southern end of the Great Barrier Reef. The reef was proved to be 378 feet thick in the Michaelmas Cay bore and fragments of coral were encountered in the underlying sands to a depth of 478 feet, indicating the presence of neighbouring reefs. In the Heron Island bore the reef was 500 feet thick, but no corals were found in the underlying sands. Hence the evidence of both bores point to a beginning of reef building from a depth of about 500 feet. Assuming that the corals commenced

at a depth of about 20 fathoms, this would indicate a sea level of about 380 feet below the present strand.

In the Heron Island bore there are two horizons of terrigenous sands which interrupted the reef building. The uppermost of these extends from 289 to 308 feet, and the lower from 386 to 405 feet. Although no terrigenous band was encountered in the Michaelmas Cay bore between 289 and 308 feet, it is notable that the zone from 241 feet to 308 feet in this bore contains no reef rock, but is made up of fine coral sand and foraminiferal sand. Reef coral is found again from 308 feet to 363 feet. From 363 feet to 378 feet the material is made up of " angular and worn fragments of calcareous skeletons, mostly calcitic coral ". Foraminiferal sand is associated with these detrital materials. Below 378 feet glauconitic and quartz foraminiferal sands were encountered to the base of the bore at 600 feet. The upper part of these to a depth of 478 feet contained pieces of clean reef coral, but below this depth no corals were found.

The sands below the coral reef in the Heron Island bore have yielded a molluscan fauna at intervals from the 500-foot level to the bottom of the bore at 732 feet. These are forms indistinguishable from living species and are regarded as being of Recent and not Pleistocene age. Their living representatives are found in shallow waters probably less than 6 fathoms in depth and certainly not more than 30 fathoms deep.

" From the coral evidence the beginning of this coral growth may have been in Recent times, but may equally have been in Plio-Pleistocene time ; for all the reef corals recognised live both today and in Plio-Pleistocene Pacific reefs. The mollusca have, however, shown that the reef rock began to form in Recent times."

The evidence of the two bores indicates that the continental shelf along the Queensland coast was deepening rapidly during Recent time, and that the sediments to a depth of 732 feet are post-glacial in age.

The two interruptions in the continuity of reef-building, and the intercalation of sedimentary deposits on the two horizons mentioned require an explanation. I suggest that these may have a climatic significance. If the temperature of the waters fell below 20° C., the corals would be exterminated and any further upbuilding during the cooler conditions would be made by sedimentary deposits.

In the Heron Island region the Fitzroy River enters the coast near by, and much more terrigenous material would be provided here than at Michaelmas Cay farther north, where the detrital material might well be supplied by the disintegration of the dead reef near by.

The chief conclusion from the point of strand line movements is the existence of a shallow water shore line as determined by the molluscan fauna, of a level within the limits of depths from about 550 to 690 feet, with a probability that the smaller figure is more nearly correct. The range suggested depends upon the range of the molluscan fauna from 6 to 30 fathoms in depth.

A summary of strand-line changes in eastern Australia has been published by Richards (1940).

New Zealand.

New Zealand lies on the true margin of the Great Pacific Basin, and like all the border coasts of this great ocean has undergone great disturbances during Tertiary time. These have continued into Pleistocene and Recent times with diminishing intensity and more local development.

In his discussion of the significance of marine terraces in New Zealand developed in post-Tertiary time, Henderson (1924) writes : " The above facts support the suggestion that New Zealand has moved in respect to sea level during later Pleistocene and Recent time as a whole. Any differential movement

between adjacent earth blocks that may have taken place during these periods must have been small, if compared to the plateau-forming movements by which New Zealand has been uplifted as a unit."

This statement emphasises the unity of New Zealand as a whole during later Pleistocene and Recent time, and makes possible a study of strand line changes in this period, whether these may be due to land or sea movements.

Sea-cut benches and marine terraces at different levels have long been recognised along the coasts of New Zealand in both the North and South Islands. Jobberns (1928) has given the most comprehensive account of the strand line movements in the South Island, where he has studied a stretch of coast about 160 miles in length extending along the eastern coast from Lyttleton in the south to the mouth of the Wairau River in the north.

In this region a study has been made of the sea-cut rock benches exposed along the coast, of raised beaches and coastal dunes, of river terraces and of upland terraces of various levels and ages. Much of the upland study is complicated by the widespread occurrence of fluvio-glacial deposits of Pleistocene age, and careful work has been necessary to establish features of undoubted marine origin.

There has been some warping and tilting due to post-Tertiary land movements, but these have been considered and allowed for in the interpretation of the strand line movements.

Much of the evidence of raised beaches and sea-cut platforms close to sea level has probably been destroyed by recent erosion, but some very impressive features remain.

Near Cape Campbell, where strongly folded marls have been planed by the sea, hard bands still stand up as reefs in places a mile distant from the shore, at heights of up to 8 feet above the general level of the platforms. At Halfmoon Bay there are a number of stacks on the lower platform, and sea-worn caves have been cut into the sea cliffs.

Jobberns considers that this evidence may be accepted as an indication " that uplift has recently taken place to the extent of at least 10 to 12 feet ".

Similar evidence is to be seen on the headlands of the Kaikoura Peninsula and Amuri Bluff.

Further south at Claverly a series of " distinct terraces, of the nature of successive former beaches can be traced across the plain ". If the first bank of shingle at an elevation of 6 feet above high water mark is taken as the upward limit of the present-day sea action, this can be compared with a second terrace standing at an elevation of 10 feet and a third of 22 feet further inland. The breadth of the latter terrace is 25 to 30 chains. A still higher terrace of more limited extent reaches an elevation of 35 feet above high water mark. The slope of all the terraces is definitely inland, and they probably represent old shingle barriers shutting off coastal lagoons behind them, " similar to that existing at the mouth of the river ". A still higher terrace remnant reaches a height of 50 to 60 feet at Conway Flat.

At 150 to 160 feet there is " a well-planed surface with terrace gravels and sands resting with a strong unconformity on a basement of grey marl ". At 250 feet, a terrace can be traced for long distances, and has a general shape of segments of circles " bearing witness to the embayed outline of the former shore . . . It extends northwards until it merges gradually into the 150-foot terrace at Amuri Bluff . . . Although a general view of the area may give a confused idea of considerable surface-irregularity, the inner edges of terrace remnants at 250 feet can be traced for long distances."

This, together with the accordance in level of the 250-foot terrace at Kaikoura, indicates that elevation was remarkably regular for many miles. Discontinuous ledges at elevations from 350 to 380 feet probably belong to

another high level terrace. At 500 to 600 feet "there is an extensive and remarkable ledge. Its seaward face is at an elevation of 550 to 575 feet and its inner edge stands at 800 feet."

Probably the most reasonable estimate represented by all these fragments is 550 feet.

Jobberns is of the opinion that there is another terrace at 650 to 700 feet, but has insufficient evidence for a conclusive statement.

Widespread remnants of a terrace at 800 feet occur for several miles south of the Conway River. These are now limited to ledges cut into the spurs separating adjacent consequent streams. Above this 800-foot terrace a well defined ledge stands at an elevation of 1,000 feet.

Some 15 miles further south at Hawkswood Bluff there is a remarkable uniformity of shore platforms and beach levels. Terraces at 40 feet and 150 feet are well marked. At one place a deposit of marine horizontally stratified beds rests on the 150-foot terrace.

Remnants of a terrace ranging from 350 to 400 feet also occur, and water-worn gravels stand at an elevation of 550 to 600 feet.

At sea level, shales tilted at high angles have been bevelled off, leaving reefs of resistant strata extending up to 400 yards off shore.

Continuing further south further evidence was found of terrace levels of 40 to 60 feet, 150 to 160 feet, 250 feet, 330 to 350 feet, 500 to 550 feet, 650 feet and 800 feet. On the coast at Sumner sea-worn caves stand 15 feet above high water mark, and in them are stratified clays with marine shells.

Jobberns has summarised his observations with regard to the higher terraces as follows :

Pleistocene or Quaternary ..	40– 60 feet
	120– 150 feet
	230– 250 feet
	330– 380 feet
Pliocene (?)	500– 525 feet
	650– 700 feet
	800– 900 feet
	1,000–1,200 feet (estimated)

He has also attempted a correlation with the terraces of the Mediterranean Sea described by Lamothe, and with other overseas evidence, but these are beyond the scope of the present lecture.

Jobberns agrees with Henderson "that any differential movements between adjacent earth-blocks are small compared with widespread emergence".

A study similar to that of Jobberns has been made by King (1930) along the south-eastern shores of the North Island of New Zealand. This covers the whole of the south coast of the island, and about 80 miles of the east coast.

In the south coast area near Port Nicholson there is evidence of a marked tilting of post-terrace age (C. A. Cotton, 1921) ; and near Wellington a vertical uplift of the coast of about 9 feet took place during the earthquake of 1855 (Lyell, 1868).

From Palliser Bay eastward, however, the terrace features have for the most part been but little disturbed by faulting, although there is a small amount of warping near the Kaiwhata River, where the terraces are well developed. Here the following terraces are recorded :

> An 8-foot terrace, probably a river terrace, exists near the mouth of the river. This is not well preserved.

> A 30-foot river terrace is well developed for 600 yards upstream. This terrace is covered by 4 feet of marine gravel, above which is a 5-foot marine bed crowded with Recent marine mollusca shells. In places the remains of trees standing *in situ* have been buried under these marine deposits. These have their roots in a Tertiary mudstone.

A second fossil forest has been revealed in the vicinity, with its roots a few feet below sea-level. This sequence indicates a rise of sea level of about 10 feet burying the older forest growing on the banks of the river, followed by a fall in sea level of 25 feet. At this stage a marine bench was cut in the Tertiary mudstone. A subsequent fall in sea level allowed a forest to grow on this bench, and a later rise in sea level submerged the second forest to a depth of several feet.

These oscillations of the strand appear more likely to have been due to changes in sea level than to movements of the land. Above the 30-foot terrace just mentioned is another river terrace at an elevation of 42 feet, and above this again another river terrace at 100 feet above sea level.

At a height of 240 feet there is a further terrace, which is warped downwards to the north to a level of 150 feet in a distance of a few miles.

At 450 feet a still higher terrace occurs, and this, too, is warped downwards northwards to a level of about 350 feet in the same distance. King (1930) considers that these warped terraces belong to the suite in the nearby Homewood district, where terraces occur at levels of 150 feet, 220 feet and 350 feet. Of these the 150-foot terrace is the best developed. North of Hawkes Bay a set of terraces occur at about 250 feet.

The warping of the upper terraces makes their correlation difficult with those of other coasts, but the 30-foot terrace beneath them is persistent over almost the whole length of the coast examined in the North Island.

In the coastal area to the west of Auckland, Bartrum has described an erosion level at 600 feet, which is widespread in the North Island and is interpreted as an uplifted peneplain of an age not earlier than late Pliocene time, since it has bevelled Pliocene sediments. A peneplain of the same elevation occurs also in the South Island where Benson has assigned to it a Cretaceous age.

Other high erosion levels recognised in the Auckland district are a 350-foot level near Oratea, and another at 120 feet which is prominent on the shores of Auckland Harbour.

The most striking erosion feature of this district is the 40 to 60-foot level. This has an unbroken length of 3½ miles at Whau Creek. A later river terrace with an elevation of 20 feet above sea level has been carved out in this terrace in the same locality.

Along the rocky headlands of the coast there are horizontal rock platforms carved out of resistant conglomerates with inclined bedding. These benches are from 2 to 4 feet above mean high water level. They are similar to the rock platforms which occur along the coast of New South Wales and many Pacific islands, such as those of Hawaii. Bartrum (1916) considers that these platforms have been cut by the sea at its present level.

While the correlation of the higher erosion levels is made difficult by warping in Pliocene, and perhaps early Pleistocene time, there does seem to be good evidence for a number of erosion levels above 100 feet in height. The lower terraces do not appear to have been much affected by faulting or warping except in local areas.

Erosion levels which are present along the coasts of both North and South Islands are:

(1) The between-tides rock platforms.
(2) A level at about 10 feet ± 2 feet.
(3) A level of 30 to 35 feet.
(4) A level of 40 to 60 feet.

Of the intermediate levels of Pleistocene age there occur in the North and South Islands:

The 150-foot level north of Hawkes Bay (North Is.).
The 150-foot level at Hawkswood Bluff (South Is.).
The 250-foot terrace north of Hawkes Bay (North Is.).
The 250-foot terrace at Kaikoura (South Is.).
The 330 to 350-foot levels of Auckland and Homewood (both North Is.).
The 350 to 380-foot terraces of Kaikoura (South Is.).

Of the higher terraces of possible Pliocene age, the 600-foot terrace of Auckland (North Is.) may be correlated with the 550 to 600-foot terraces of Kaikoura and Hawkswood Bluff of the South Island.

Less evidence is available from New Zealand with regard to stands of the sea below present sea level, but recent submergence is well recognised. Borings at Auckland revealed a submerged channel estimated to be not less than 150 feet deep.

In the Fiordland region of the south-west of the South Island, King and Jobberns (1933) record drowning of the fiords to a depth of 200 feet.

East Indies.

Passing northwards from Australia into the South-west Pacific we find along the northern margin of the continent a broad and shallow floor of the ocean basin known as the Sahul Shelf. This extends northwards to New Guinea. Little is yet known of its detailed submarine topography. It is thought, however, from its general characteristics, that it is a submerged region of Pleistocene age. Its origin may perhaps be similar to that of the Sunda Shelf which has been studied by Molengraaff (1922) and Umbgrove (1929).

The Sunda Sea lying between Borneo, Sumatra and Java has, as the result of many soundings, had its submarine topography well mapped. In such detail, indeed, as to make it possible to trace across its floor the course of a drowned river system which Molengraaff has called the North Sunda River. Before its submergence it flowed across a peneplain (the present Sunda Shelf) and received tributaries from northern Sumatra and western Borneo. This river system is now submerged to a depth of about 100 metres. The submergence is confirmed by a study of the fresh-water fish fauna of northern Sumatra and western Borneo, which are closely related. The course of the North Sunda River is north-easterly to the edge of the Sunda Shelf, where this is bordered by the South China Sea (Krempf and Chevey, 1933). A similar submerged river system lies between south Borneo and Java, where it trends in a south-easterly direction. The amount of submergence here has been traced to about 90 metres. The whole of this region is shown by geological investigations to have been stable during late Tertiary and Pleistocene time.

The Philippine Islands.

Northwards along the western Pacific beyond Borneo lies the archipelago of the Philippine Islands. There is evidence that in Pleistocene time the main Philippine Islands were united as one great island and that its low-lying lands

have been since submerged to a depth of about 50 metres (Faustino, 1926). The chief elements of this submerged terrain are the Babuyan Shelf north of Luzon, the Polillo Shelf east of Luzon, the Visayan Shelf surrounding Palawan Island, the Leyte-Samar Shelf east of Leyte Island and the Sulu Shelf west of Mindanao. One of the largest of these is the Babuyan Shelf, which is a northward prolongation of Luzon Island. It is 140 kilometres long from north to south and 80 kilometres wide, and has an average depth of a little more than 50 metres. Series of terraces are common on many of the islands. These have been described by Feliciano and Pelaez (1939).

One or more terraces have been found on all the larger, and on many of the smaller islands. These are best known or seen on Luzon, Leyte, Mindinao and Cebu. In age they range from Pliocene to Pleistocene. A slight difference in tilt between those of Pliocene and Pleistocene age is seen in Cebu and Leyte. Most of the terraces are marine in origin.

A study of the freshwater fishes shows that the Philippine Islands have been united during the Pleistocene, and the occurrence of two species common to southern China and the Philippines points to a land connection with the mainland during Pleistocene time.

The dominant recent movement has been one of submergence.

The greatest number of terraces observed in a single sequence is seven. These occur in southern Cebu and north-western Pangasinan (Fanning, 1912). Where there is a sequence of terraces they are found to be concordant, being parallel to one another, and generally parallel to the present shore line.

Most of the Philippine terraces are level or slightly tilted. The older ones have suffered considerable erosion, but can be identified by concordant levels of the dissected terrace remnants.

The Pleistocene deposits exhibit considerable variety, and marine conglomerates and elevated coral reefs as well as river terrace deposits have a widespread distribution. Igneous activity in Pleistocene time is represented by basalt and andesite lava flows, and accumulations of agglomerate.

Block faulting has taken place to some extent in Pleistocene time, but the concordance of terrace levels in general appears to indicate that such movements are of a local character.

The majority of the terraces are of Pleistocene age, but the higher terraces were probably formed in Pliocene time. No precise level of demarcation between the Pliocene and Pleistocene terraces is recorded.

The following table gives the numbers of terraces recorded, and shows their geographical distribution.

The best sequences in one district are:

Luzon (Bolinao-Pangasinan district): 50, 110, 150, 200, 250, 320, 380 feet.

Cebu (Ginatilan district): 150, 250, 450, 590, 780, 990, 1,160 feet.

Leyte (Rabin Point): 15, 100, 200, 350 feet.

Luzon (San Fernando-La Union district): 70, 250, 300 feet.

Luzon (Bamban-Tarlac district): 100, 120, 200 feet.

It will be seen from this analysis that the most widespread levels are those at

100– 110	feet on Luzon and Leyte.
200	feet on Luzon and Leyte.
240– 250	feet on Luzon and Cebu.
590– 600	feet on Luzon, Cebu and Mindinao.
990–1,000	feet on Cebu and Mindinao.
1,160–1,200	feet on Cebu and Mindinao.

TABLE OF PHILIPPINE TERRACES.

Terrace Levels Feet above Sea Level.	Geographical Distribution.	Number of Separate Localities.
15	Leyte	1
30	Luzon	1
50–60	Cebu	3
70–80	Luzon	2
100–120	Leyte, Luzon..	10
150	Cebu, Leyte and Luzon ..	3
200	Leyte, Luzon..	8
240–250	Cebu, Luzon	4
275	Luzon	1
300–320	Leyte, Luzon..	4
350	Leyte	1
380–400	Luzon, Bohol	2
450	Cebu	1
480–500	Luzon, Bohol	2
590–600	Luzon, Cebu and Mindinao	5*
650	Mindinao, Masbate	2
780–800	Cebu, Luzon	2
900	Mindinao	1
990–1,000	Cebu, Mindinao	4
1,160–1,200	Cebu, Mindinao	9*
1,300	Mindinao	1
1,900	Cebu	1

* On Mindinao five terraces are recorded at 600 *or* 1,200 feet. Only two of these are included in this table.

Formosa.

An account of the post-Tertiary history of Formosa is given by Hayasaka (1933). In the last stages of the Tertiary, Formosa appears to have been part of the Asiatic continent. This connection may even have extended into early Pleistocene time, since fossil remains of rhinoceras have been found in Formosa in beds of this age.

At the end of the Pliocene a submergence of Formosa to at least a depth of 1,000 metres is indicated, and this was followed by an emergence marked by many halting stages which are now represented by marine terraces. Raised reefs of Pliocene limestone are strongly tilted, and these are capped unconformably by Pleistocene deposits which are but slightly inclined. The extreme north of the volcanic peak of Daiton, built up chiefly by lava flows, is surrounded by a series of marine terraces. Seven such terraces occur at successive elevations of 50 metres, 100–150 metres, 200–250 metres, 300 metres, 350–400 metres, 500 metres and 600 metres.

The terraces at 200–250 metres and at 350–400 metres occupy considerable areas, and the latter is the best developed of the whole series.

Another mountain peak lying to the south-west of Mt. Daiton is also terraced. This is Mt. Kwauninzan, which is 612 metres high. The terraces on this mountain are at elevations of 50 metres, 100 metres, 150 metres, 200 metres and 250 metres.

It has not yet been found possible to correlate these with the terraces at Mt. Daiton. None of the terraces represents the surface of lava flows.

There is in northern Formosa a bench level of 100 metres which has a wide extent, and this is correlated with the 100–150 metre terrace at Mt. Daiton. Running along the foot of this 100-metre terrace is another at a level of 40 metres

which may correspond to the 50-metre terrace of Daiton. A still younger terrace from 5 to 10 metres high is recognised in northern Formosa.

In south-eastern Formosa terraces flank the coastal range on its seaward side. Here a 100-metre terrace is recognised, and a lower terrace of from 20–30 metres is terminated seawards by a cliff 10 metres in height.

In the southernmost part of the island lower terraces of 5 to 10 metres have been recognised. These are found also in many other places in the island, including the northern area. They are formed by the upper surfaces of late Pleistocene, and perhaps Recent coral reefs.

Studies of the sea floor by Yabe and Tayama (1929) revealed a submerged system of river valleys which were traced to a depth of about 700 metres. For the most part the strait of Formosa does not exceed 50 fathoms in depth.

Japan.

Yabe (1933) states that marine terraces of Pleistocene age " are developed in varying degree almost everywhere throughout the Japanese islands from Sakhalin at the north to Taiwan (Formosa) at the south ".

Although block faulting is prevalent, and is still active, the later movements " are recognisable only by reference to these several datum planes ".

Five terraces are recorded by Tsujimura (1926) from the island of Okujiri, which lies off the west coast of Hokkaido, the northernmost of the Japanese islands.

Drowned river valleys and dissected coastal plains are typical features of the physiography. The unity of these is broken by faulting and warping, but these are local discordances.

On the main island, Otuka (1933) has recorded a marine terrace some 20 metres above sea level in the region about Tokyo. Terraces from 30 to 80 metres above sea level are found on the central part of this island facing the Sea of Japan. Higher terraces at 60 and 100 metres also occur here. The lowest marine terrace is three metres high. Drowned valleys are characteristic of this part of the coast. This area has been described by Mochizuku (1933). Ohashi (1933) has studied the physiography of the Dewa district in north-western Honsu, and in spite of block faulting movements has recognised from three to five broad terraces, the highest of which has an elevation of 300 metres. Next in importance are the terraces at 60 and 100 metres.

In the southern island of Kyushu, Yamane (1933) has recognised two main terrace levels. The lower one is marked by raised beaches and sea-worn caves. Above this stands a Pleistocene erosion level of 50 to 100 metres which has been dissected by stream erosion. The latest movement is one of submergence.

China.

Little information is available along the China coast, but studies by Barbour (1926) of stream rejuvenation in north-east China in post-Pliocene time point to a former stand of sea level above the present level.

Along the south Manchurian coast he has described marine terraces 40 metres above sea level. Borings at Shanghai encountered a limestone conglomerate at a depth of 902 feet. Shell fragments thought to be marine were encountered at a depth of 280 feet in wells close to the bore site. Wells sunk at a distance of 150 miles from the coast at Chu-lu-Hsien passed through 500 feet of unconsolidated sediments.

In the Yunan valleys at least six stages in terracing have been detected.

Korea.

The Tertiary and post-Tertiary history of Korea has been studied by Kobayashi (1933), who recognised coastal terraces ranging from 50 to 100 metres

high facing the Sea of Japan. Corroborative evidence is provided by river terraces along the Kan-ko valley.

Subsidence of great magnitude is shown by the drowned valleys of Kyojo.

Kamchatka and the Aleutian Islands.

An extensive plain of marine denudation up to a mile or more in breadth is well developed about Cape Japounski, where it has been recorded by Dawson (1894). This rises inland to a height of 700 to 800 feet from its seaward edge, which stands 600 feet above the sea. This upland has been dissected by stream erosion to depths of from 50 to 100 feet. The valleys at the coast do not reach sea level, but appear as hanging valleys along the sea cliffs.

On the east side of the harbour of Petrapavloosk a marine terrace is discernible at a height of 250 feet.

A number of the Aleutian islands have also been described by Dawson. The chief features of these are given as follows :

On Unalaska Island, the little village of Unalaska is built on a gravel covered terrace standing about 20 feet above high water mark. This is regarded as being of marine origin.

On the northern side of the island a mountain which terminates in a promontory is flanked by a series of terraces at least three in number. The highest of these stands at an elevation of 1,000 feet.

On Attu Island gravel terraces 20 to 30 feet above sea level flank the coast. The slopes of the hillside rising from Chichagof harbour bear several faint terrace remnants, the highest of which stands at 300 feet.

The southern shores of Behring Island at Nikolski are bordered by a well marked terrace 20 to 30 feet above the high tide level.

Copper Island shows several definite terraces, the highest of which is 600 or 700 feet above sea level.

A narrow terrace borders the north shore of Cape Vancouver at a height of 80 to 100 feet above sea level. This is probably a marine terrace.

On the eastern side of Saint Laurence Island a fairly distinct terrace is preserved at a height of 50 feet above sea level. This has been cut back in granitic rocks as a narrow step.

Alaska.

Marine benches and river terraces are widely distributed along the Alaskan coastal area. Some of these, as for example the raised beach at Yakutat Bay, are due to fault displacements.

Buddington (1927), who spent five field seasons studying the Alaskan coast, has recorded many features which he attributes to changes in the strand levels. He states that " One of the most conspicuous and outstanding features of the coastline of south-eastern Alaska, south of the Icy Straits and Cross Sound, is the frequent occurrence of an abandoned rock bench at an elevation approximately that of the present high tide level, ranging from a few feet below to a few feet above ".

The recency of this bench is indicated by a glacial polish which is still preserved on it in places even where still " exposed to the full force of the Pacific swells ". In some places, as at Suemez Island, many stacks standing on such a marine bench are found.

A rock bench of from 12 to 16 feet in elevation occurs at Totem Bay, where it is carved in a Tertiary rhyolite, and at Glacier Bay, where the range is from 12 to 16 feet. The same level occurs at Frederick Island near Point Agassiz, where a large gravel terrace stands 20 feet above low tide level. Dall has recorded a raised beach at Nome standing at 22 feet, and another which extends

inland somewhat less than a mile and reaches an elevation of 37 feet. In the same locality a still higher raised beach lies $2\frac{1}{2}$ to $3\frac{1}{2}$ miles inland and stands at an elevation of 79 feet.

At Gravina Island fossiliferous gravels and clays lie at 80 feet above sea level.

Knopf (1912) has observed fossiliferous marine gravels near the mouth of the Eagle River, which are now 100 feet above sea level.

A still higher bench ranging from 160 to 200 feet has been seen by Buddington on the islands of the Keku group. These benches form wide flat surfaces. This level is also represented by fossiliferous clays and gravels on the Stikine River, about five miles above the international boundary. These range in elevation from 175 to 200 feet.

High level river gravels standing 300 feet above the present river occur along the Salmon River, which is here 150 feet above sea level.

Buddington states : " Benches and terraces of fossiliferous marine gravels, sands and clays are found locally at various altitudes up to 600 feet throughout southern Alaska." One of these standing at 600 feet occurs at Juncan, where it has been described by Spencer.

A Recent change in sea level along the Alaskan coast is one of submergence to a depth of about 20 feet. Depressed beaches at this level have been proved by boring at Nome by Moffit (1913) and a submerged forest at Glacier Bay at a depth of 20 feet is recorded by Buddington.

The deeper submergences of some 300 feet found elsewhere in the Pacific are obscured by the presence of the deep fjords due to glacial action.

Canada.

Along the northern part of the Canadian coast glacial overdeepening in the fjords reaches 2,000 feet according to Peacock (1935), who, however, describes submarine valleys extending to 1,000 feet in depth, which he regards as being due to submergence. Evidences of raised strand lines occur up to an elevation of 600 feet. These are of post-glacial origin.

Along many parts of the coast from Vancouver to Alaska there are rock platforms between tide levels. These in places are up to 1,000 feet in breadth.

Johnston (1921 and 1926) records raised post-Glacial delta deposits at an elevation of 50 feet on the Fraser River at a distance of 30 miles from the coast. He also has found at Wrangell, Ketchikan, Prince Rupert and Port Simpson a number of " abandoned beaches at various heights above the sea ". Most of these have been carved out of glacial drift.

Both to the north and south of the Fraser River there are uplands reaching a general elevation of from 200 to 400 feet.

At Vancouver, a series of glacial deposits has been found to have interbedded in it a fossiliferous marine horizon which now stands 50 feet above sea level. The shells in it are similar to or identical with those living between tide levels in the vicinity. Similar shell-beds have been found here at various heights extending upwards to 350 feet.

Well-terraced delta deposits are found at the mouths of streams flowing into Burrard Inlet. These occur at elevations up to 650 feet.

Deep submergence has been proved by borings which have passed through Pleistocene and Recent deposits to a depth of 860 feet below sea level. These borings were made near the mouth of the Fraser River. Similar borings in the Nicomekl-Serpentine Valley passed through post-glacial clays to a depth of 300 feet.

The United States.

The city of Portland, Oregon, is built on a series of terraces of the Columbia River. The highest of these stands at an elevation of 300 feet. This terrace has been dissected and another developed out of it at a level of 200 feet. High level terraces are found for a considerable distance upstream. The chief of these is " The Great Terrace ", which stands between 600 and 700 feet above the present valley floor. It has been suggested that this was formerly part of a great delta front. As the present valley floor here is 670 feet above sea level, this high terrace may imply a total elevation of as much as 1,370 feet. Bretz (1919), who has described this region, has also deduced high stands of sea level in the Columbia River valleys from the positions of erratics which have been left stranded by melting icebergs. These erratics cannot be attributed to the action of glaciers. The highest of them stands 1,200 feet above present sea level.

The region lies at a distance of 150 miles from the margin of the Pleistocene Ice Cap, and Bretz states that the cause of the elevated strand cannot be attributed to isostatic warping following the melting of the Pleistocene ice. The 300-foot terrace at Oregon is correlated with that which occurs at Puget Sound.

Strand line changes along the coast of California have long been known, and have been described by Lawson (1893) for the region extending from San Francisco to San Diego. Here many post-Pliocene strands occur, extending upwards to 1,500 feet above sea level.

The coast along the Bay of Monterey is beautifully terraced in the vicinity of Santa Cruz. Three great terraces at elevations of 96, 205 and 712 feet extend with a marked horizontality for 15 miles to the west and north-west of the town. A fourth terrace at 374 feet has been observed in places between the two higher terraces, but this appears to have a more limited development. The altitudes given were made on the extreme landward side of the terraces where they are highest. Each terrace has a slight seaward slope, and at its seaward margin is terminated by an old sea-cut cliff. Near their seaward fronts the terraces are sparingly covered with sea-worn pebbles.

The rocks in which the terraces are carved are of Miocene age and these rest unconformably on metamorphic rocks intruded by granite. The Miocene sediments dip seawards at low angles, but the terraces are cut at a still lower angle and bevel the edges of the Miocene outcrops. This feature is constant over the whole of the terraces and is conclusive evidence of marine transgression and erosion.

The rapidity of the " uplift " is remarkable, for the canyons cut in the higher terraces before the movement have not yet had time to entrench themselves in the lower terraces.

The lowest terrace ranges from half a mile to a mile in width, and exceeds in breadth that of the second terrace, which is less than half a mile wide. Many higher terraces occur, and these are all strewn with water-worn pebbles, but the mantle of vegetation which covers them renders them less prominent to the eye. Lawson's observations were made by aneroid barometer and include nine terraces at levels given at 1,201, 1,133, 1,025, 969, 871, 712, 374, 205 and 86 feet above sea level. No mention is made of lower strands. Some 400 miles southwards near San Diego a terraced plain from 12 to 18 miles wide is described. The seaward cliff margins of the terraces are similar to those of the Monterey system. This whole region is described as a Pliocene delta into which stream action has developed a system of river terraces adjusted to different stages of sea level. True sea-cut terraces also occur. The geological history of the delta is complex and no detailed study of it has been undertaken. The upper surface of the Pliocene delta which was adjusted to sea level now stands at an elevation of 800 feet.

No attempt was made to measure the elevation of all the stream terraces. The highest noted has an elevation of 675 feet and a breadth of 300 yards. A narrower terrace stands at 600 feet. From this level downwards " remnants of stream terraces may be found at many different levels ".

Corresponding to the stream terraces there are a number of well defined wave-cut terraces. The lowest of these has in places a width of several hundred yards, and has been found at several localities between San Diego and San Luis Rey River.

The highest sea-cut terraces have been found only on Saledad Mountain, where they " are strikingly well preserved ". The more important of these massive terraces occur at elevations of 700, 600, 520, 340 and 160 feet. These levels are based on aneroid observations.

There are along the coast of California three topographic forms having a linear arrangement along a length of about 50 miles, which have yielded a rich harvest of terrace remnants. These are San Pedro Hill and San Clemente Island studied by Lawson and the intermediate island of Santa Catalina studied by Tangier Smith (1933).

San Pedro Hill is a land-tied island which would be completely separated from the mainland by a submergence of 150 feet. It is a flat-topped hill washed on three sides by the sea. It is characterised by " the great system of terraces which score the hill like giant steps ". Each terrace is bounded seawards by an ancient sea-cut cliff. In addition, stream cut terraces occur and these are canyoned above the 240-foot terrace.

The marked horizontality of the terraces is an impressive feature.

The marine origin of the terraces is established by the borings made in the rocks by marine molluscs, and these were observed up to an elevation of 1,240 feet. Measurements were made at the highest levels of the terraces where they were bordered by steep-walled cliffs of the next higher terrace. Eleven terraces were found and their respective elevations are given as 1,240, 1,040, 960, 860, 700, 550, 400, 300, 240, 160 and 120 feet. The hill rises to 1,475 feet but no terrace was observed above the 1,240 foot level.

During most of its history San Pedro Hill has been an island.

To the south-west of San Pedro Hill and at a distance of about 50 miles lies the island of San Clemente. Like San Pedro this is a flat-topped ridge, but somewhat higher, rising to 1,964 feet. Along its south-western side a wonderful series of seventeen great terraces adorn its slopes. The highest reaches an elevation of 1,320 feet. They " appear to be of amazingly recent formation ", and are mostly of bare rock, and slope gently seawards.

The terraces range from 200 to 1,500 feet in breadth, and the heights of their sea-cut cliffs from 50 to 300 feet. On other sides of the island similar terraces occur with the same vertical intervals, but here they are not so well developed. In particular, the trail from Wilson's Cove to the summit crosses eighteen such terraces, two of which exceed in elevation the 1,320 foot terrace on the south-western side. The altitudes given are tabulated as follows for comparison.

The heights of the terraces on the south-western side were estimated to the nearest 40-foot contour of the Coast Survey Map, but those of Wilson's Cove section appear to have been made by aneroid measurements. No terrace was observed above the 1,500-foot level.

San Clemente Island is volcanic in origin and consists of lavas and breccias with some bands of limestone. It is probably not later than Miocene in age. The bedding is generally inclined, and the terraces truncate the strata.

Lawson remarks that " the full number of these stages is probably greater than is now registered in the elevated strands of the island ".

TERRACES OF SAN CLEMENTE ISLAND.

From Wilson's Cove.	South-western Side.
1,500	—
1,375	—
—	1,320
1,250	1,240
1,040	1,040
960	960
930	—
785	800
—	680
580	—
550	560
470	480
—	440
380	400
325	320
—	280
225	200
170	160
120	120
85	80
40	40
12	—

To ascertain the effect of wave cutting, the maximum breadth of seventeen prominent terraces was measured, and their aggregate sum is two miles. The strands of San Clemente Island agree well with those of San Pedro Hill.

Santa Catalina Island was subjected to a cursory examination but Lawson found no evidence of strands on this island, and commented on the anomaly.

A subsequent detailed study of Santa Catalina by Tangier Smith (1933) has shown, however, that this island is also strongly terraced.

The evidence of coastal terraces yielded by Lawson's work covers a range of about 400 miles but this does not extend to the limit of such features. Lawson concludes that " the facts adduced in the present paper establish a recent uplift of the continental margin, from the Golden Gate to San Diego, of from 800 to 1,500 feet. The geographical extent of the uplift is not measured by the range of the observations here recorded. There is evidence that the uplift extends far to the south and far to the north of the coast subjected to inspection. The uplift is clearly epeirogenic in character."

In a former publication Lawson (1893*a*) has described terraces at the northern end of the Santa Monica Mountains at elevations of 570, 460–480, 300, 150–160 and 25–30 feet above sea level.

Along the coast of California fronting the Santa Lucia mountains Trask has measured terrace levels at 380, 245, 167, 123 and 40 feet above sea level.

Davis (1933) considers that some warping has taken place along this coast and correlated the 40-foot level of Trask with that recorded by Lawson at 25–30 feet. Davis also describes two terrace levels extending along some 30 miles of coast fronting the Santa Monica Mountains. The higher of these standing at an elevation of 200 feet he has named the Malibu platform, and the lower, at 100 feet, he has called the Dume platform. Mention is also made of two other platforms, but he does not give their elevation, and places them below the Malibu platform. Davis considers that the Dume terrace is to be correlated with the

40-foot terrace of Trask. If this is correct some warping has taken place along the coast in this area.

Tangier Smith's work on Santa Catalina Island is based on four types of criteria for changes in the strand. These are :

(1) The notched salient.
(2) The elevated embayment.
(3) Accordant summits.
(4) Marine deposits.

The rocks of the island are very resistant, consisting of metamorphic types and massive quartz diorite porphyry, and it is for this reason that the terraces are not so well developed as those described by Lawson.

Tangier Smith, by the application of the criteria adopted, has established a great succession of terraces at levels of 1,680–1,720, 1,600, 1,520–1,500, 1,440–1,480, 1,320–1,360, 1,240–1,280, 1,080–1,120, 960–1,000, 800–840, 680, 520–560, 440–480, 360 and 240 feet.

The levels were determined to the nearest 40-foot contour of the Coastal Survey Map. A small marine deposit of shell fragments and rolled pebbles was found at an elevation of 1,400 feet.

These observations are in good agreement with those of Lawson at San Pedro Hill and San Clemente Island.

Putnam (1937) has recorded four major terraces on the south-west slope of Rincon Mountain 15 miles west of Ventura. These stand at elevations of 1,300, 1,100, 800 and 500 feet. Local warping has displaced the levels so that the lowest terrace rises from 210 feet at its western end to 570 feet at the eastern in a distance of three and a half miles. This terrace is the broadest of the series, having a width of 0·3 mile. It is fronted by a sea cliff 570 feet high.

Deep submergence along the Californian coast is also recognised. Fairbanks (1897) points out that the Santa Barbara Islands are connected with the mainland by a submarine ridge the lowest part of which is 750 feet below sea level. In the early Pleistocene deposits of the island fossil bones of the mammoth have been found, and hence at this period there must have been a connection with the mainland. This clearly indicates a submergence of at least 750 feet since early Pleistocene time.

The continental shelf broadens from a width of 10 miles in the north to 150 miles off southern California. Here the charts show submarine valleys cut into the continental shelf and extending downwards to a depth of 500 fathoms. This is considered by Fairbanks to indicate deep submergence. He specifically states that the idea thay they have been downfaulted is rejected as being untenable.

Branner (1907) states that in the neighbourhood of the Santa Clara river " the dendritic topography of the submerged valleys shown by the hydrographic charts is so characteristic of land-forms produced by stream erosion, that there is no escaping the conclusion that they were formed when the region was out of water ". The evidence of the freshwater fishes in the coastal streams points to their having been formerly part of one river system the lower part of which is now submerged.

As the origin of submarine canyons is still a matter of controversy it may be wise to suspend judgment as to their sub-aerial origin.

Davis (1933) considers that there is evidence of submergence due to the passing of the last phase of the Pleistocene Ice Age, and this view has been repeatedly advanced by Daly (1925, 1929, 1935) for the whole of the oceans.

South America.

Strand line changes along the Pacific coast of South America have long been known. Darwin was greatly impressed by the clearness of the evidence, and has given the best general account of them in his Journal of Researches.

The *Beagle* followed southwards along the eastern coast of South America and passed to the Pacific Ocean by the Straits of Magellan, after which the vessel followed the Pacific coast northwards.

Darwin had found unequivocal evidence of a series of marine terraces along the Atlantic coast from Rio Plata to southern Patagonia. He states that " the land from the Rio Plata to Tierra del Fuego, a distance of 1,200 miles, has been raised in a mass (and in Patagonia to a height of between 300 and 400 feet) within the period of now-existing sea-shells. The old and weathered shells left on the surface of the upraised plain still partially retain their colours. The uprising has been interrupted by at least eight long periods of rest, during which the sea ate deeply back into the land, forming at successive levels the long lines of cliffs or escarpments which separate the different plains as they rise like steps one behind the other . . . the lowest plain is 90 feet high ; and the highest which I ascended near the coast, is 950 feet." It was therefore with this background of experience that Darwin continued his studies of strand line displacements along the Pacific coast of South America.

He reached Conception shortly after a great earthquake, during which the land round the Bay of Conception had been elevated some two to three feet.

At Valparaiso he examined " great beds of shells, which stand some yards above the sea " and further states that " the proofs of the elevation of this whole line of coast are unequivocal ; at the height of a few hundred feet old-looking shells are numerous, and I found some at 1,300 feet ".

Inland from the coast there are a series of coastal mountain-chains, separated from the main cordillera by " a succession of level basins, generally opening into each other by narrow passages ". Darwin observed that when these basins were covered by a fog-bank they strongly suggested a former connection with the sea. He writes : " These basins or plains, together with the transverse flat valleys (like that of Quillota) which connect them with the coast, I have no doubt are the bottoms of ancient inlets and deep bays such as at the present day intersect every part of Tierra del Fuego and the western coast."

At Portillo Pass (from Santiago) he found a similar topography. The river valleys descending from the Andes converged here into these inland basins. The valleys carried on their flanks well developed terraces. Of these Darwin says, " No one fact in the geology of South America interested me more than these terraces of rudely stratified shingle . . . It is impossible here to give the reasons, but I am convinced that the shingle terraces were accumulated, during the gradual elevation of the Cordillera, by torrents delivering at successive levels their detritus on the beach-heads of long narrow arms of the sea, first high up in the valleys, then lower and lower down as the land slowly rose."

At Coquimbo he investigated the raised beaches first noticed by Captain B. Hall. Here " five narrow, gently sloping, fringe-like terraces rise one behind the other, and where best developed are formed of shingle ; they front the bay, and sweep up both sides of the valley ".

At Guasco north of Coquimbo the terraces are developed on a grand scale " so as to strike with surprise even some of the inhabitants ". Here the terraces are much broader and extend inland to a distance of thirty-seven miles.

One well marked marine terrace at Coquimbo contains recent species and has an elevation of 250 feet. This deposit rests on beds of Tertiary age which extend " for 1,100 miles on the Pacific coast and 1,350 miles on the shores of the Atlantic ".

Writing of northern Chili Darwin says, " I have convincing proof that this part of the continent of South America has been elevated near the coast at least from 400 to 500, and in some parts from 1,000 to 1,300 feet, since the epoch of existing shells ; and further inland the rise possibly may have been greater ".

There is historic evidence that at Valparaiso there has been a local rise of the coast to nearly 19 feet in the past two hundred and twenty years. At Lima there is a raised beach some 80 to 90 feet high which is stated to have been elevated during the Indo-human period.

Off the coast of Peru, on the island of San Lorenzo, opposite the Bay of Callao, there are three obscure terraces. The lower of these has been traced for a mile in length. It stands at an elevation of 85 feet. It contains eighteen species of shells now living in the adjacent sea. On an upper terrace at 170 feet there are deposits of sulphate of lime similar to some found associated with the shell bed at 85 feet. Similar deposits of sulphate of lime were found at a still higher level and are regarded as evidence of a higher stand of the sea.

Darwin examined the 85-foot terrace and found embedded in the shell deposits pieces of cotton thread, and the head of a stalk of Indian corn. This is taken as evidence of the recency of these deposits, for which, however, there is no historic information.

Darwin in his Geological Investigations (1876) records shell banks at Iquique at elevations of 150 and 200 feet.

Orbigny (1842) reported recent marine shells some 300 feet above sea level.

Evans (1907) has noted raised beaches at Taltal in northern Chile on the coastal plain which rises inland to a height of 200 feet. A lower bench exists at 80 feet and a third is seen along the shore line at 15 feet above sea level. The latter is marked by shell banks, and a line of shallow caves.

Douglas (1920) has found abundant remains of a raised beach at Mollendo, in Peru, at a height of about 50 feet above high water mark.

Bowman (1909) in the same country has found recent marine shells embedded in a clay bank at an elevation of 800 feet. Further inland he describes " gently sloping rock benches of huge size, formed by the sea and subsequently elevated to 1,500 feet. Along the inner margin of these, terrace coves are to be found, like those seen at many places on the present strand line, or but little above it."

The preceding account of strand line changes in the Pacific has dealt only with the lands and island chains bordering this great ocean. Consideration will now be given to the islands which lie within its borders.

The Hawaiian Islands.

This group of islands is entirely of volcanic origin, and of pre-Pleistocene age. It extends in a north-westerly direction for about 1,000 miles. The chief islands are those which form the south-eastern members of the group. Their elevated strand lines and submerged features have been studied by Stearns (1935*a* and 1935*b*).

Earlier studies were made by Wentworth and Palmer (1925), who stated that " a bench from 4 to 12 feet above mean sea-level exists on all the islands of the Hawaiian chain, without exception ". They conclude that the evidence supports a former stand of the sea from 12 to 15 feet above present sea level. Pollock (1928*a* and 1928*b*) considered that a rise of sea level of 15 feet would not have been sufficient to cut the benches on Oahu and that a rise of 20 feet would have been needed.

Stearns (1935*a*) has made a detailed and quantitative examination of the shore line features of Oahu. On Kapapa Island, on the northern side of Oahu, he describes two rock benches. The lowest lies between tide levels, being about a foot above mean sea level. The higher bench is from 3 to 6 feet high and 75

feet wide, and is swpet by storm waves from time to time. A pronounced notch made in the sand beach stands 9 feet above sea level. Blocks of limestone up to 4 feet in diameter have been carried by storm waves across the bench. The bench is pitted by weathering, and from this condition Stearns concludes that the bench is not being actively cut by present-day storm activity.

On Moku Manu Island a remarkably level bench from 3 to 8 feet high and 150 feet wide is carved out of a steeply dipping basaltic tuff. This bench is only awash during heavy seas. There is a well marked notch at the foot of the cliff bounding its landward side. On the windward side there is a deposit of well-rounded beach cobbles at an estimated elevation of 30 feet above sea level. This is taken as evidence of a former sea strand 25 feet above present sea level. On the leeward side of Oahu, near the mouth of the Nanakuli valley, outcrops of limestone occur some 25 feet above sea level. Along the shore there is a rock platform between tides, and a bench from 5 to 7 feet above mean sea level. This is storm swept, and a recent storm has banked up on it beach sand to some 10 feet above mean sea level.

At Waimea there are two benches, as at Nanakuli. On Mokuhooniki Island there are two benches, the lower being 1 to 3 feet and the higher 5 to 8 feet above mean sea level. The same two benches occur on Manana Island. On the mainland opposite, a large sea-worn cave stands 25 feet above sea level. This is completely beyond wave action, and is accepted as evidence of a sea stand about 25 feet above present sea level. At the entrance to Hanauma Bay two benches occur, the lower at 6 feet, and the higher from 10 to 12 feet above mean sea level.

Further studies by Stearns (1935*b*) on the islands of Oahu and Maui have yielded evidence of higher strand lines during Pleistocene time. These were found at elevations of 25, 40 (?), 55, 70, 95 and 250 feet above present sea level.

These findings are based upon a number of features including wave-cut benches, marine terraces in sediments at the mouths of valleys, emerged reef limestones, loose marine detritus, consolidated beach deposits and nips in lithified dunes.

The highest level of 250 feet is best shown on Maui, where a well cemented marine fossiliferous beach conglomerate occurs up to 240 feet above mean sea level.

A possible strand, at least 150 feet above sea level, is indicated by black muds, apparently marine, in the Lualualei valley, Oahu.

The 95-foot level is well developed on both Oahu and Maui. At Kaena, on Oahu, a lava boulder beach well cemented by calcareous sand contains coral pebbles and fossils. This stands 89 feet above sea level.

A fossiliferous reef limestone occurs at Waianae at a level of 97 feet above sea level. The heights were determined by precise levelling.

On Maui extensive gravel fans occur which are graded to the 95-foot level.

The 70-foot stand of the sea is best seen near Laie, on Oahu, where a lithified dune sand is found resting upon a pebbly fossiliferous beach sand, which is 71 feet above sea level. A practically continuous reef some 4 miles long and half a mile wide extends across the mouth of the Lualualei Valley, and this was found by precise levelling to be 72 feet above sea level. This reef is terminated seaward by a precipitous cliff, with its base 25 feet above sea level. This escarpment was cut by waves of the 25-foot stand of the sea. Hence the 70-foot stand is older than the 25-foot strand line.

Similar evidence of the 70-foot level is found on Maui.

The evidence for the 40-foot stand of the sea is found only on Oahu. Many terraces occur at this level but the only evidence of their marine origin is the presence of loose marine shells found at an elevation of about 45 feet above sea level.

The 25-foot strand is so well marked that " nearly every geologist subsequent to Dana has called attention to it ". The most convincing evidence actually points to two levels, one at 22 feet and the other at 27 feet above present sea level. Near Waimanalo lithified dunes have been notched by two regular incised parallel nips one above the other which are continuous for several thousand feet. These are 22 and 27 feet above present sea level.

Near Pui Mailiilii a terrace has been cut at the foot of a cliff 8 feet high, and a wave-cut bench 5 feet wide lies above this cliff. These features agree with those of the nips in the lithified dunes at Waimanalo.

Benches and shore features of a sea about 25 feet are almost continuous around Oahu. Wave-cut benches and marine terraces at about 25 feet are also common on the west coast of Maui.

In addition to elevated strand lines in the Hawaiian Islands there is also abundant evidence of submergence.

Profile studies of the ocean floor off the shores of West Maui, Lanai, Molokai and Oahu show that an extensive shelf occurs at about 1,800 feet below sea level. Stearns (1935*b*) has suggested that this represents the upper surface of a coral reef and that this was developed at about the present level of the ocean and subsequently submerged.

A submergence of at least 1,200 feet is indicated by bores on Oaho.

A remarkably level shelf standing from 300 to 360 feet below present sea level surrounds Oahu, Maui and other islands of the Hawaiian group. This attains a breadth of nearly two miles off Kaena Point, Oahu.

A stand of the sea some 60 feet below present sea level has been determined at Pearl Harbour, where the bottoms of the drowned valleys are graded to about this level. This is confirmed by an extensive submarine platform surrounding Oahu at a depth of about ten fathoms. This stage of sea level is later than the 95-foot strand and was preceded by the formation of the 25-foot strand.

South-west Pacific.

The war-time activities of the United States afforded an unprecedented opportunity for the examination of the topographic features of the islands over a large part of the South-west Pacific.

The most comprehensive studies on shore-line changes in this region are those made by Stearns (1945) on the New Hebrides Group.

On the island of Espiritu Santo the remnants of a high level terrace about 1,200 feet above sea level appears to be the oldest and highest recognised. This probably is the same as that noted by Mawson (1905) and estimated as at least 1,000 feet high. Small remnants of a terrace were also observed at a height of 650 feet ; and other narrow terraces were seen between this and the 1,200-foot terrace, but their altitudes were not determined.

The most extensive terrace is that which, covering many square miles, stands 560 feet above sea level. The terrace materials consist of a fossiliferous coral reef and reef detritus. The bedding is horizontal. This terrace extends along the eastern side of the island for a distance of 30 miles. Measurements made with a dumpy level show that the terrace is not tilted. It has been partially dissected by stream action which has in places cut into the terrace to a depth of about 30 feet. It usually carries a soil layer from 6 to 8 feet in thickness covering a pinnacled limestone basement.

A narrow terrace which may be either a river or marine terrace has a limited development at 480 feet.

Terrace remnants of accordant height have been seen in a few places at levels of about 375 feet.

Another broad terrace rises from 290 to 340 feet on its landward side, and this may be the seaward sloping tread of the 375-foot terrace. Narrow terraces observed at 300 feet also fall within this group.

Another prominent feature of the landscape is a terrace standing a little above 260 feet. This in places is nearly a mile in breadth. It has been cut into by the sea at levels of 225 and 215 feet. The latter level is marked by a notch cut in the limestone cliffs. Still another terrace has been cut into the 260-foot terrace at a level of 150 feet.

At a still lower level a prominent terrace at 100 feet occurs along the southern and western shores of the island. It is, however, much more narrow than the 260-foot terrace. A sea cave at 95 feet on the near by Aore Island may correspond to the 100-foot terrace on the main island.

A very narrow terrace at a level of 45 feet has been cut into the 100-foot terrace. A typical notch corresponding to this stand of the sea is a prominent feature. It is several feet deep and several hundred feet long. The apex of the notch stands 48 feet above mean low water, which is here 2·9 feet below mean sea level. As this notch faces a channel free from storms, it may be taken as a precise level of the sea stand which cut it.

The most prominent of the low level terraces is that which forms a bench up to half a mile wide. Numerous sea-worn caves of large size also mark this stand of the sea. The best estimate of this level is 27 feet above the present mean sea level.

Many remnants of coral reefs standing 5 feet above sea level fringe the island. These are seldom more than 10 yards wide. They are notched at their base by the action of the present sea. Numerous abandoned sea caves and notches confirm this 5-foot stand of the sea.

Fossil corals and molluscs have been collected from all the terrace levels from 560 feet to the lowest. The similarity of these to those of the known Pleistocene and Recent fauna from other parts of the Pacific appears to indicate that they are not older than Pleistocene. The materials have been sent to the National Museum for identification, and the final age limits must await confirmation. It is, however, possible that the 560-foot terrace may be of late Pliocene age.

None of the limestones forming the terraces has been disturbed, and they rest horizontally on the eroded surfaces of folded Tertiary sediments.

Stands of sea level which are now submerged occur at levels of 60 and 300 feet below present sea level. The 300-foot submergence is marked by the drowned canyons of the Sarakata and Renée Rivers. These have been partly filled by coral debris and delta deposits.

Along the south coast, a narrow submarine shelf occurs at depths of from 10 to 12 fathoms. The outward edge of this shelf plunges steeply to depths of 30 to 50 fathoms.

Other islands in the New Hebrides, e.g. Efate and Malelula, carry well-defined flights of horizontal terraces.

In the Solomon Islands Group a well preserved suite of horizontal terraces are to be seen in Guadalcanal Island. The most prominent of these are the two which stand at 560 feet and 260 feet above sea level. Another terrace at 150 feet is also clearly defined in places. The reef coral limestone forming the terrace lies undisturbed on warped and faulted shales and marls of Tertiary age. At Mt. Austin the limestones reach a height of 1,200 feet.

In the Marianas Islands well defined terraces have been studied in Saipan Island. Several terraces standing above 260 feet were observed, but as terraces due to faulting in Tertiary limestones are common, the higher Pleistocene terraces could not be distinguished with certainty. The terrace at 260 feet is well marked, and extends for several miles along the eastern coast, bevelling the

folded Tertiary strata. It is the most extensive and prominent of the known Pleistocene terraces.

Next in height is the 140-foot terrace which has been cut into steeply inclined thin bedded limestones. This terrace is backed by a wave-cut cliff.

At Obram Point a sea-worn notch is preserved in the sea cliff at 100 feet above present sea level. This is matched by an extensive sea-cut terrace at the same level near by. Another terrace has been found at 70 feet.

On the southern coast of Saipan there is a prominent terrace at 45 feet which in places is up to a quarter of a mile in width. This has been cut across an older limestone, and terminates landwards in an abandoned sea cliff full of caves. The 25-foot terrace is also well defined, and the terrace at 5 feet above present sea level is the lowest of the series. It is marked by deep notches cut into the cliffs fronting the sea.

Stearns states that he has flown over all the islands from New Caledonia to Guadalcanal and has seen horizontal limestone terraces extending for miles on the islands in this area.

Suess (1900) accepted the emerged coral reefs of the Loyalty Islands as proof of a former sea stand of 330 feet above the present sea level.

Stearns has found a barrier-reef formation in New Caledonia at an elevation of 375 feet.

In Guam, Rota, Aguijan and Tinian Islands suites of horizontal terraces are recorded by Stearns, but their elevations have not so far been determined.

An account of the marine terraces of the islands south of Japan under the Japanese mandate has been published by Tayama (1939) in which a table has been drawn up correlating the terrace levels in these islands. The chief islands are those of the Marianas and Caroline Groups. They are divided into a western island group including the Marianas and an eastern island group containing the Carolines.

The geological age of the terraces is given where possible. Many of the higher terraces are of Tertiary age. Those of Plio-Pleistocene and Recent age are given below, the heights being in metres.

(*a*) *Western Island Groups.*

Pagan	A terrace at 1–2 metres.
Medinilla	Terraces at 80 and 50 metres, and a raised notch.
Saipan	Terraces at 130, 90, 60, 40, 30, 20, 5 and 1·5 to 2 metres.
Tinian	Terraces at 170, 150, 110, 80, 60, 45, 25, 10 and 1·5 to 2 metres.
Aguigan	Terraces at 180, 160, 80, 45, 30, 10 metres, and a raised notch.
Rota	Terraces at 480, 460, 420, 380, 300, 260, 200, 180, 140, 100, 80, 60, 40, 20, 10 and 3 to 4 metres.
Yap	Terraces at 10 and 1 to 2 metres.
Palau	Terraces at 220, 120, 100, 70, 50, 40, 20, 10, 7, 1 to 2 and 2 to 3 metres.
Angaur	Terraces at 50, 20, 10 and 2 to 3 metres.
Merir	Terraces at 1 to 1·5 metres.

(*b*) *Eastern Island Groups.*

Fais	Terraces at 23, 20, 15, 10, 5 and 1 to 2 metres.
Truk	Terrace at 1 to 2 metres.
Ponape	Terrace at 1 to 2 metres.
Kusai	Terrace at 1 to 2 metres.
Jaluit	Terrace at 1 to 2 metres.
Pokaak	Terrace at 2 to 3 metres.

Some of the terraces which are stated to be of Tertiary age range from 30 to 200 metres and others rise to as much as 470 metres. These have not been included in this review as strand line changes of Tertiary age are not being considered in this paper.

Fiji and Tonga.

Andrews has shown that many terraces occur in the Fiji Group. Six of these are illustrated by a section of Yathata, given in the report of Agassis' expedition (1900, p. 22). No measurements were recorded of the staircase-like profiles to be seen on these islands.

Ladd and Hoffmeister (1927) have described what they consider to be an upraised fringing reef on Vitilevu, some 30 feet wide and standing at an elevation of 6 feet above the highest tide level. Behind this is a sea-cut cave standing at the foot of a cliff about 15 feet high. The floor of the cave is 5 feet above the level of the highest tide. These workers consider that there has been here a recent shift of the sea of at least 6 feet.

Along the whole of the western side of the island of Eua in the Tonga Group an old fringing reef stands from 2 to 4 feet above the reach of the highest tide. As at Vitilevu this reef is of recent age. On the island near the town of Ohonua there is in a sea-flooded ravine a cave the floor of which is 9 to 10 feet above the high tide level. To be correlated with this evidence is a well defined sea-cut nip standing 8 feet higher than a similar nip now being cut at the base of a cliff some 30 feet high. This evidence is taken to indicate a 9–10 foot recession of the sea.

The island of Tongatabu, lying north of Eua, has an elevated coral reef, covered with calcareous algæ and serpulite tubes which stands from 10 to 15 feet above the high tide level.

It is stated that " all of the islands of American Samoa are likewise surrounded by a shore bench, which according to Mayor (1924) is about 10 feet above present sea level ".

Chamberlin (1924), who collaborated with Mayor, estimated that these benches indicated a sinking of sea level of from 12 to 15 feet. Daly (1924), however, has observed that the cliffs now being cut in Samoa by the present sea have depths of about 12 feet of water at their bases at high tide and from this he estimated that the recession of sea level may be about 20 feet.

The *Austral Islands* have been studied by Chubb and Smith (1927), who recognise a shelf standing about 3 feet above high water mark and backed by sea-worn caves on the island of Maiao. On the island of Rapa a bench encrusted by lithothamium stands at an elevation of 6 feet above the present sea level and lies at the foot of a sea-cliff composed of limestone. This extends to 100 feet above sea level.

On the island of Rurutu limestone has been found at altitudes up to 400 feet. Above this stands an upland plateau at 800 feet above sea level. Two other levels are recognised below it at elevations of 600 feet and from 200 to 300 feet. Raised benches indicating an uplift of from 6 to 8 feet are recorded, and shore platforms of limestone which suggest an elevation of from 1 to 2 feet are also recorded.

At least two stages of submergence are suggested by submerged coral reefs at depths of from 8 to 15 fathoms about Rurutu Island, and by the presence of a fairly extensive submarine platform up to a mile in width, at a depth of about 30 fathoms, surrounding the island of Rapa.

Conclusion.

In this survey of strand line changes in the Pacific Ocean there is a striking degree of correspondence extending over large areas. This is manifested not only along the continental shores but among the chief island groups.

A summary of the evidence is given in Tables I and II.

In Table I the strand lines ranging from —100 to +100 feet are given.

In Table II the strand lines from +100 to +650 feet and from —100 to —600 feet are recorded.

From these, Figures I and II have been prepared.

TABLE I.

Terrace Levels Recorded between +100 Feet and −100 Feet within the Pacific Region.

South America.	California.	Canada.	Alaska.	Aleutian Islands and Kamchatka.	Korea and China.	Japan.	Formosa.	Philippines.	New Hebrides.	Solomon Islands.	Marianas and Caroline Islands.	Fiji and Tonga.	New Zealand.	Hawaii.	Austral Isles.	South-Eastern Australia.				
																N.S.W.	Victoria.	South Australia.	Queensland.	Tasmania.
			100					100	100		100		100			100				
						98	98													
	96													95						
																		90		
85																				
																		to		
	80		80					80			80					80		80		
								to			75					75				
								70			70			70						
						65	65				65							65		
								60					60							
																		to		
								to					to	55		55 to				
50	50	50		50				50			50	Many higher terraces.	50			50		50		50
									45		45			45						
	40												40			40				
			37																	
													35			35				
							32				32		to							
	30			30				30					30			30				
	to								27					27		to				
	25									25	25			25		25				
			22											22				25		
				20									20			20			20 to	
			16 to 12				16				16									
15								15				15		15 to 12		to		to	15 12	15
						10					10-13 7-10	9–10	10–12			10 8		10	8	
													6–8		6–8		8			
									5	5	5					5–6	to	5–6	5–6 3–4	5
			3											3–8	3					
												2–4	2–4			2–4	2			
									SEA	LE	VEL									
													−10							
															−15	−15				
																−36				
																−50				
									−60					−60						
																−70				
																−90				

TABLE II.

Terrace Levels Recorded between +100 to +650 Feet and −100 to −600 Feet within the Pacific Region.

South America.	California.	Canada.	Alaska.	Aleutian Islands and Kamchatka.	Korea and China.	Japan.	Formosa.	Philippines.	New Hebrides.	Solomon Islands.	Marianas and Caroline Islands.	Fiji and Tonga.	New Zealand.	Hawaii.	Austral Isles.	South-Eastern Australia. N.S.W.	Victoria.	South Australia.	Queensland.	Tasmania.
	680																			
		650					650	650	650		650		650							
	600	600	600	600				600 to 590					600		600					
											590									
	560 to 520					Some higher terraces.			560	560	560		550 to 500							
											525									
500 to 400								500 to 480								500 to 400				
							490				490									
	480 to 440								480											
								450			460		450 to 400							
											430	A number of higher terraces—at least six.								
	400							400 to 380			400				400					
	380 to 360												380							
									375											
											360									
	350 to 340	350						350					350 to 330							
									340											
					330	330	330				330									
	320							320 to 300												
	300	300	300	300					300		300				300					
	280																			
								275												
						260			260	260	260									
250								250 to 240					250	250				250 to 160		
	240																			
									225 to 215											
													220							
200	200	200	200 to 160	Several terraces.	Six stages known in China.			200			200					200				
						200														
170																				
					165		165				165									
	160 to 150																			
150								150	150	150	150		150	150(?)		150		150 to 120		150
											140									
					130		130				130					130 to 120				
	120							120 to 100												
			100						100		100		100			100				
									SEA	LEV	EL									
													−150							
								−165												
															−180					
													−200							
																−250				
									−300					−300						
														−360						
																			−380	
																−400				
																			−550	
																			−690	
							−700													
	−750																			
		−860																		

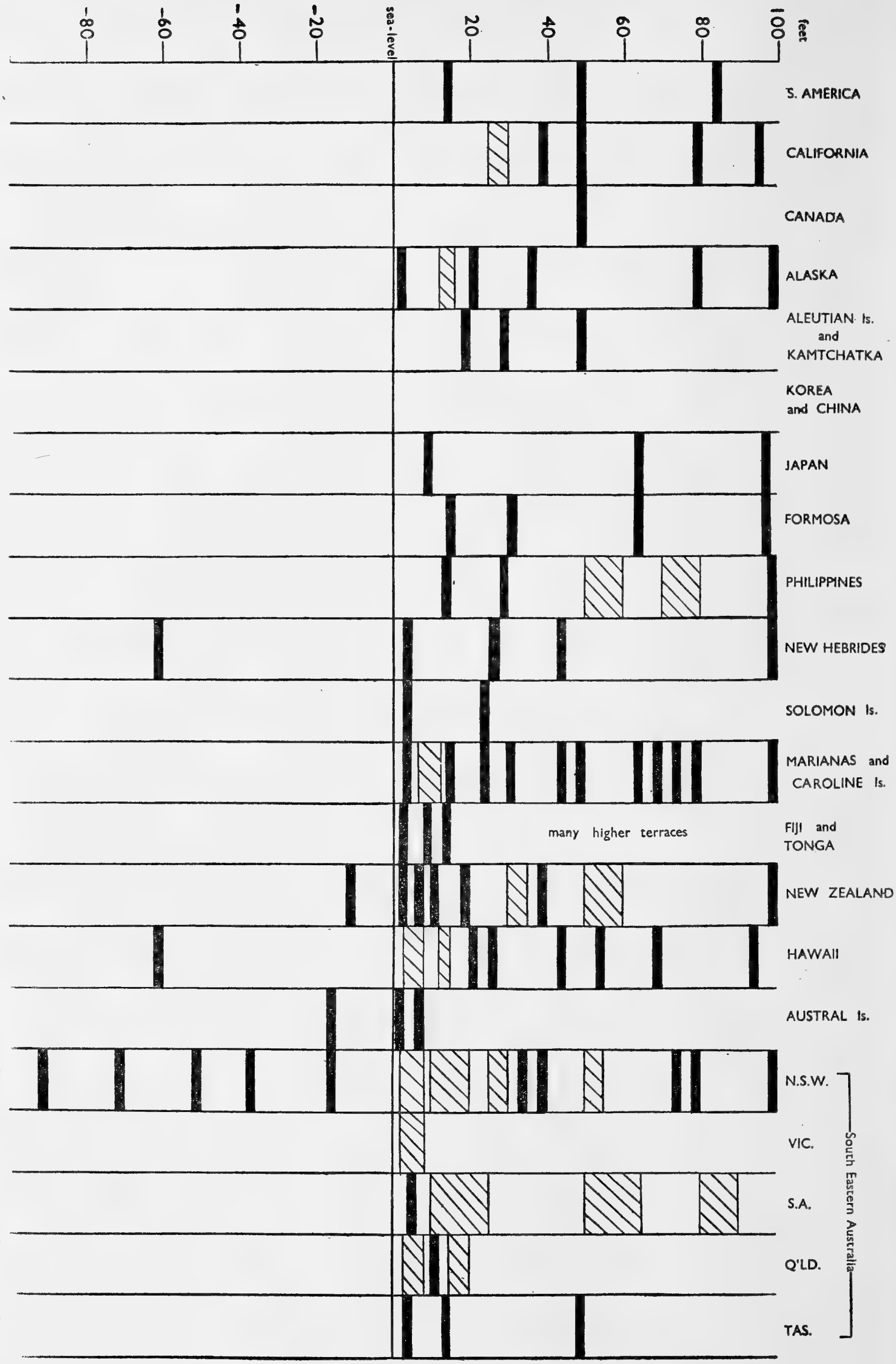

Fig. 1.—Distribution of terrace levels around the margins of the Pacific Ocean and of the islands within its bounds between +100 and −100 feet.

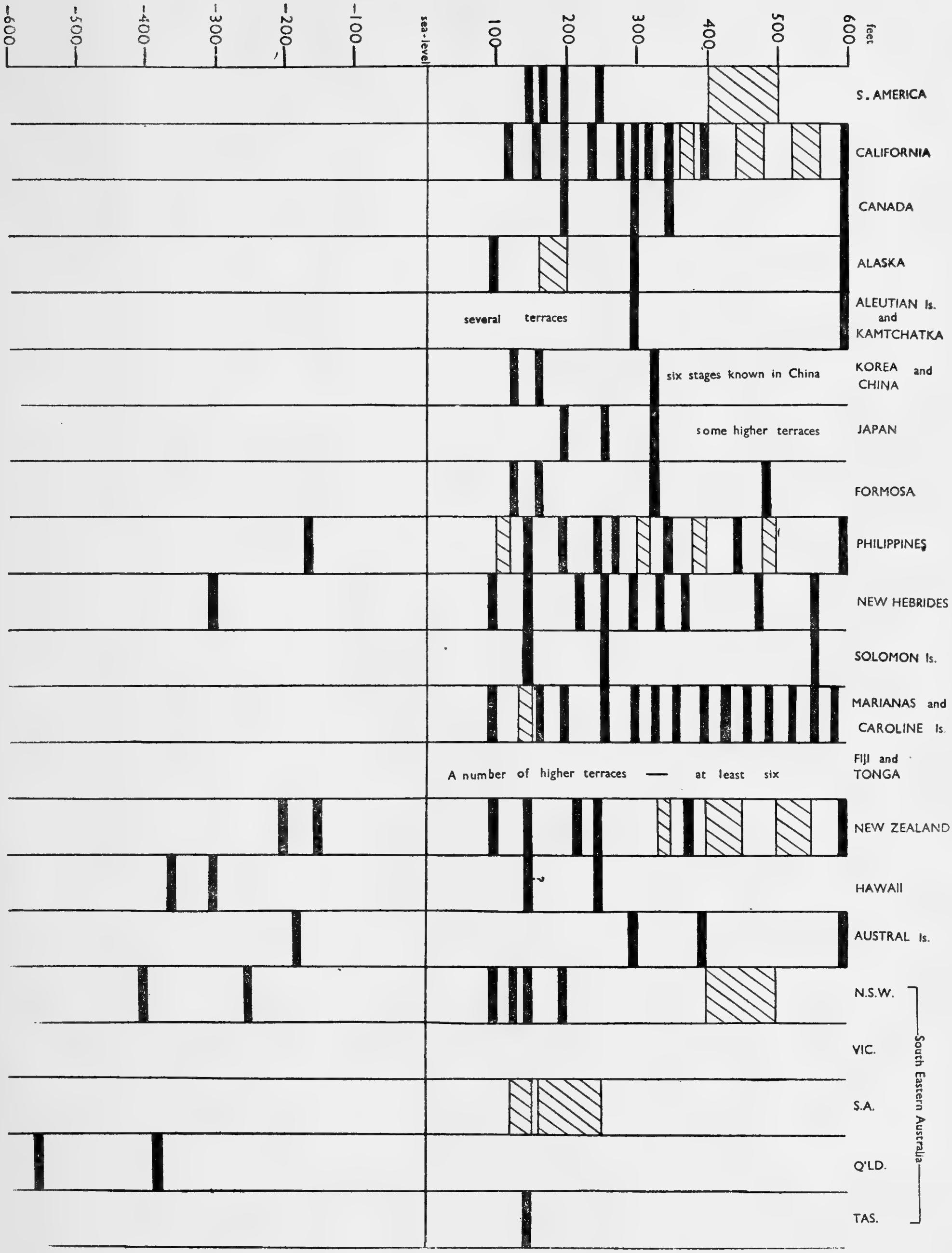

Fig. 2.—Distribution of terrace levels around the margins of the Pacific Ocean and of the islands within its bounds between 100 to 650 feet and −100 to −600 feet.

The study of Figure I shows that certain levels have a wide distribution throughout the Pacific Ocean. The chief of these are the strands at 5, 10, 15, 25, 45 and 100 feet above sea-level. In Figure II the levels having the widest spread are those at about 100, 150, 200, 250, 300, 340 ± 10, 400, 490 ± 10, 560 and 600 feet in elevation.

It should be remembered that many, and probably most, of the observations have been made by aneroid barometers. These are seldom precise instruments, and in any case are subject to errors due to fluctuations of barometric pressure during the period of the observations. The absence of records of some of these levels in areas lying between those which do exhibit them is not necessarily proof that the sea did not stand at the same level over the whole area. Rocks vary in their degree of resistance to wave attack. Some aspects of the sea front may be protected, e.g. those behind a fringing or barrier reef. Again, terraces or benches may have been cut in soft rocks and since completely eroded.

In some places the features may exist but have so far escaped observation. Where there is an absence of any trace of benches in rocks which are suitable for their formation and preservation, this negative evidence must be taken into account in any attempt to explain the existence of such features over large areas of the Pacific Ocean.

Many records of terraces exceeding 600 feet in elevation are known, but many, if not most of these antedate the Pleistocene period, and do not come within the scope of this investigation.

The lack of data for terraces above 250 feet in Hawaii and Japan, and the abundance of terraces above this level in California, the Philippine Islands, the New Hebrides, the Marianas and Caroline Islands and New Zealand, suggests that these may have been overlooked in Hawaii and Japan. It is hoped that the attention drawn to this may stimulate further investigation in these islands.

The paucity of records of submergence is to be expected from the nature of the phenomena associated with them, and there is not sufficient evidence yet available to form a sound basis for discussing such features.

Strand line changes can be due only to movements of the land or movements of the sea. It is unlikely that movements of the lands of the same vertical range could extend over very large areas, for such movements as have been proved are usually accompanied by warping.

Vertical movements of the sea, on the other hand, would affect the whole surface of the oceans, and if displacing them to the same extent, the movement would be eustatic.

The widespread occurrence of many of the terrace levels shown in Figure I and Figure II points to changes in sea level due to movements of the sea. In these figures elevations and submergences exceeding 600 feet have not been included, as these in general are older than Pleistocene in age.

The fluctuations of the polar ice caps during Pleistocene time has been offered by Daly (1925, 1929 and 1935) as an explanation of strand-line changes. The order of the movement probably does not exceed 200 feet in elevation or 300 feet in depression (Antevs, 1930; Zeuner, 1945 and 1946).

The correlation of the chronology of glacial and interglacial epochs of the Pleistocene time with strand line changes of an eustatic character has been examined in great detail by Zeuner (1945, 1946).

For strand line movements of a greater vertical range than ± 300 feet some other cause must be sought; and for these Stearns (1945*b*) has suggested four possibilities. These are as follows:

(1) Changes in the configuration of the ocean basins.
(2) Volume changes within the earth's crust giving rise to expansion and contraction (cf. Joly, 1925).

(3) Outpouring of lava on the ocean floor and subsequent isostatic adjustments.

(4) Continental drift.

But at least one other possible cause deserves consideration. Polar wanderings have been discussed (Cotton, 1923), Wegener (1924). The effect of these on the ocean level would not be eustatic in character, but for small movements the effects would approximate to eustatic displacements. For larger polar displacements vertical movements might range over thousands of feet in the areas where the movement was at its maximum.

The purpose of this paper has been to collect and correlate the evidence of strand line changes in the Pacific Ocean. There is a great deal of similar evidence along the shores of the other great oceans, and any attack on the problem of the causes of such movements must take these into account. For this reason the investigation of the fundamental causes of strand line changes must be left until a world-wide survey of such movements has been completed.

In conclusion I wish to express my thanks to Miss M. Breckenridge for assistance in the preparation of the figures, and for much help with the bibliography; and to Mr. N. C. Stevens and Mr. B. P. Webb for bibliographical research.

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SOME DISUBSTITUTED DIPHENYL DERIVATIVES.

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In an attempt to prepare 3-nitro-4′-methoxydiphenyl (I) by a Gomberg reaction between diazotised *m*-nitroaniline and anisole, using the sodium acetate modification of Elks, Haworth and Hey (1940), the only pure product isolated was the isomeric *3-nitro-2′-methoxydiphenyl* (II), although the presence of (I) was undoubted. Other modifications of the above reaction using (*a*) *m*-nitro-N-nitrosoacetanilide and anisole (Grieve and Hey, 1934 ; France, Heilbron and Hey, 1939) and (*b*) the stabilized diazonium salt, formed from *m*-nitroaniline and naphthalene-1 : 5-disulphonic acid, and anisole (Hodgson and Marsden, 1940) also gave (II) in approximately the same yield. Owing to the simpler technique required, the first method is recommended as the most convenient process.

The constitution of (II) was determined by catalytic reduction to the amine (III) followed by diazotisation and deamination with hypophosphorous acid (Kornblum, 1941) ; the liquid 2-methoxydiphenyl (IV) being identified by two solid derivatives.

Certain other derivatives of *3-amino-2′-methoxydiphenyl* were prepared and are described in the experimental section.

Having obtained this somewhat unexpected *ortho* orientation with anisole two further amines, aniline and *p*-anisidine, were coupled with it with similar results. (IV) was obtained in fair yield from aniline but the yield of 2-4′-dimethoxydiphenyl from N-nitroso-*p*-acetanisidide (V) was very small.

This latter result is in contrast to the 55% yield of 4-methoxydiphenyl obtained by Grieve and Hey (*loc. cit.*) from (V) with benzene.

Harley-Mason and Mann (1940), in a Gomberg reaction between *p*-bromoaniline and anisole, report a 20% yield of 4-bromo-2′-methoxydiphenyl and a 7% yield of 4-bromo-4′-methoxydiphenyl. This is the only case where yields of isomers are quoted in the literature when anisole is the second component of the reaction.

Although toluene, nitrobenzene and mono-halogenated benzenes have been used many times as the second component in the above reactions, the isomeric diphenyls obtained have been separated only in the case of nitrobenzene and toluene. With one exception nitrobenzene directs predominantly to the *para* position. In the only case where the isomers obtained with toluene were separated the orientation was predominantly *ortho*. The case of nitrobenzene may be explained by the hindrance to the *ortho* positions by the large nitro group.

No explanation can be offered for the results with anisole, but it is intended to use substances like tertiary butyl phenyl ether as the second reactant to see if this would hinder the *ortho* positions.

It should be pointed out that the statement in " Organic Reactions ", Vol. II (Ed. Adams, 1944) that nitrobenzene reacts more rapidly than toluene in Gomberg type reactions is misleading. It is apparently based on the result that if *o*-nitrotoluene is used as the second reactant the diphenyl is 3-methyl-4-nitro substituted, that is the phenyl group is joined to the position

para to the nitro group. This agrees with the theory that there will be more resonance in the activated complex when the nitro group is *ortho* or *para* to the point of attack but it does not necessarily prove the reaction is faster with nitrobenzene than with toluene. The evolution of nitrogen does not, of course, give a measure of the rate of reaction, but only of the formation of free aryl radicals. The result with *o*-nitrotoluene does suggest that by no means every collision between the radical and solvent is effective, and it would be interesting to know the collision efficiency in such reactions.

It was also intended to couple *m*-cyano-N-nitrosoacetanilide with anisole but the former could not be prepared, only the diazonium salt being obtained by the usual nitrosation procedure. Grieve and Hey (*loc. cit.*) have reported similar results with certain other acetylated amines.

EXPERIMENTAL.

3-Nitro-2′-methoxydiphenyl (II). (*a*) *By Sodium Acetate Method.*

m-Nitroaniline (69 g.) and concentrated hydrochloric acid (160 c.c.) were mixed, cooled and diazotised in the usual manner with a solution of sodium nitrite (35 g.) in water (90 c.c.). The filtered diazonium salt solution was vigorously stirred with anisole (750 c.c.) and a mixture of sodium acetate (160 g.) in water (400 c.c.) was added dropwise, the temperature being kept below 10°. Intermittent stirring was continued over a period of 48 hours, the first three at below 10° and the remainder at room temperature. The success of the experiment depends on good mixing of the two layers. The anisole layer was separated, washed with water, dried over anhydrous sodium sulphate, anisole removed and the residue distilled under vacuum, 58 g., i.e., 50% yield of a pale yellow oil was obtained, b.p. 180°–182°/2 m.m., which solidified on cooling and was purified by a second distillation followed by recrystallisation from methanol. It formed very pale yellow prisms m.p. 66°.

Found: C, 68·2; H, 5·0%. Calculated for $C_{13}H_{11}O_3N$: C, 68·1; H, 4·8%.

(*b*) *By Nitrosoacetylamine Reaction.*

m-Nitro-N-nitrosoacetanilide was prepared by the method of France, Heilbron and Hey (*loc. cit.*) except that the nitrous fumes were generated from sodium nitrite and nitric acid as Haworth and Hey (1940) recommended. The creamy-yellow emulsion and oil obtained on diluting the reaction mixture with iced water was extracted with anisole, the extract washed quickly with water and then kept over anhydrous sodium sulphate for 36 hours (during which time nitrogen was evolved). After filtration the excess anisole was removed and the residue vacuum distilled. The yield of (II) was 47% based on the *m*-nitroacetanilide used.

(*c*) *By Stabilized Diazonium Salt Method.*

A stabilized diazonium salt of *m*-nitroaniline was formed with naphthalene-1 : 5-disulphonic acid in a manner similar to that of Hodgson and Marsden (*loc. cit.*). The dry stabilized diazonium salt was suspended in anisole and decomposed with fused sodium acetate and acetic anhydride. After standing for 48 hours it was heated to 80° to complete the reaction. The mixture was diluted with water, the anisole layer separated, washed with sodium hydroxide solution and dried over calcium chloride. Yield of (II) based on stabilized diazonium salt used was 50%.

3-Amino-2′-methoxydiphenyl (III).

(II) was reduced to the amine by shaking an alcoholic solution at normal pressure and room temperature in an atmosphere of hydrogen in the presence of Raney nickel, when the theoretical amount of hydrogen was absorbed. After filtering off the catalyst, the alcohol was removed and the residue vacuum distilled. Yield, 75%. B.p. 175°/1·4 m.m. or 184°/3·5 m.m. It solidified on cooling and crystallized from ethanol as white prisms m.p. 70·5°–71°.

Found: C, 78·5; H, 6·7%. Calculated for $C_{13}H_{13}ON$: C, 78·2; H, 6·5%.

3-Acetamido-2′-methoxydiphenyl.

Acetylation of (III) with acetic anhydride in the usual manner gave the acetyl derivative which crystallized from ethanol as white prisms m.p. 132°–132·5°.

Found: N, 5·9%. Calculated for $C_{15}H_{15}O_2N$: N, 5·8%.

3-Benzamido-2′-methoxydiphenyl.

Benzoylation of (III) with benzoyl chloride and sodium hydroxide gave the benzoyl derivative which crystallized from ethanol as white truncated prisms m.p. 121°–122°.

Found: N, 4·6%. Calculated for $C_{20}H_{17}O_2N$: N, 4·6%.

N-(2 : 4-Dinitrophenyl)-3-amino-2′-methoxydiphenyl.

When (III) (1 g.) and 2 : 4-dinitrochlorobenzene (1 g.) were heated in a boiling water bath until the melt solidified (about 15 minutes) the N-2 : 4-dinitro-phenyl derivative was formed. Recrystallized from ethanol (500 c.c.), it formed a mixture of orange needles and slightly lighter orange stout prisms. The prisms were separated from the needles fairly readily by fractional recrystallization as they were much less soluble in alcohol. The separated prisms were then recrystallized from benzene. Both the prisms and the needles melted at 200°–201° and a mixed melting point of the two showed no depression.

Found (Prisms): N, 11·4%; (needles): N, 11·4%. Calculated for $C_{19}H_{15}O_5N_3$: N, 11·5%.

Apparently the products are merely different crystalline forms of the one substance.

2-Methoxydiphenyl (IV).

(III) (6 g.) and concentrated hydrochloric acid (14·7 c.c.) were mixed, warmed, then cooled and diazotised with sodium nitrite (2·4 g.), dissolved in a little water, in the usual manner. After filtration the ice-cold diazo solution was added to an ice-cold solution of potassium hypophosphite (26·4 g.) and concentrated hydrochloric acid (29·5 c.c.). After standing overnight in the refrigerator and then at room temperature for 24 hours the dark liquid was extracted with ether. The ethereal extract was washed well with dilute sodium hydroxide solution, then water, dried over anhydrous potassium carbonate, filtered and distilled. 4 g. (i.e. 72%) of an almost colourless oil with a sharp fruity odour b.p. 128°/3 m.m. were obtained.

2-Methoxydiphenyl has b.p. 159°–160°/18 m.m. or 274°/760 m.m. and melts at 29°. It has a fruity, slightly pungent, aromatic odour. 4-Methoxydiphenyl has m.p. 90°.

Nitration of the oil in a manner similar to that of Borsche and Scholten (1917) gave yellow needles from ethanol m.p. 91°. 5-Nitro-2-methoxydiphenyl (VI) forms yellow needles m.p. 95·2° (corrected) (Borsche and Scholten, *loc. cit.*).

Further nitration of (IV) with a boiling mixture of acetic and nitric acids (as Hill and Hale, 1905), yielded a white product, crystallizing from ethanol, m.p. 171°. 3 : 5 : 4′-Trinitro-2-methoxy diphenyl has m.p. 170°–171° (corrected) and would be the expected trinitration product of (IV).

From this evidence the deamination product must be 2-methoxy diphenyl; therefore the amine obtained from the Gomberg reaction must have been 3-amino-2′-methoxydiphenyl.

2 : 4-Dimethoxydiphenyl.

Solid N-nitroso-*p*-acetanisidide (V) was prepared by the method of France, Heilbron and Hey (*loc. cit.*) m.p. 82°–83°. It was treated with anisole in a manner similar to that which they used with benzene. From 18 g. of (V) a large quantity of a black tar was obtained. Vacuum sublimation of this tar gave white crystals which after recrystallization had m.p. 65°–66°. 0·5 g. of the recrystallized material was obtained; no other product could be isolated in a pure condition. 2 : 4′-Dimethoxydiphenyl forms white crystals m.p. 70° and 4 : 4′-dimethoxydiphenyl white crystals m.p. 173°. The product obtained in this reaction therefore was 2 : 4′-dimethoxydiphenyl.

2-Methoxydiphenyl (IV).

Benzene diazonium chloride solution prepared from aniline (10 g.) in the usual manner was treated with anisole (50 c.c.) and sodium hydroxide (9 g. in 30 c.c. of water) by the general method

given by Grieve and Hey (*loc. cit.*). The product was purified by vacuum distillation. It was a pale, only faintly lemon coloured, oil with a fruity odour b.p. 130°/4 m.m. Yield 15% based on aniline used. Nitration of the oil by the method of Borsche and Scholten (*loc. cit.*) yielded pale yellow needles m.p. 91° which did not depress the melting point of the 5-nitro-2-methoxydiphenyl formed from the deamination product of (II). The product isolated from this reaction was therefore 2-methoxydiphenyl.

Summary.

Gomberg type reactions with *p*-nitroaniline and anisole yielded 3-nitro-2′-methoxydiphenyl in 50% yield. No other product could be isolated. Reduction to the amine was effected with hydrogen and Raney nickel. Derivatives of the amine are described. The identity of the amine was established by deamination to 2-methoxydiphenyl which was identified by means of its nitration products. The reaction between N-nitroso-*p*-acetanisidide and anisole gave only a poor yield of 2 : 4′-dimethoxydiphenyl, while the action of nitrous fumes on *m*-cyanoacetanilide failed to yield an N-nitroso derivative. 2-Methoxydiphenyl was obtained by means of a Gomberg reaction between benzene diazonium chloride and anisole.

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Part III

STRATIGRAPHY OF WESTERN AUSTRALIA.*

By CURT TEICHERT, D.Sc.

With Plates IV-VII and ten text-figures.

Communicated by DR. W. R. BROWNE.

Manuscript received, July 17, 1946. Read, August 7, 1946.

ABSTRACT.

The State of Western Australia covers about one-third of the Australian continent, that is almost a million square miles. As far as known not less than one-third of this area is underlain by sedimentary rocks, not including the Precambrian. All the major geological systems are represented, with the exception of the Silurian, but the occurrence of Triassic is doubtful. The stratigraphical sequences and the distribution of sedimentary rocks are described according to periods, beginning with the Cambrian and proceeding to the Pleistocene. Eventually, the sedimentary areas are classified according to their significance and grouped in the following categories : (1) scattered outcrop areas, (2) large, comparatively thin sheets, (3) coastal basins, (4) major basins. Thicknesses in (1) and (2) do not exceed 2,000 feet. Basins of group (3) are little known, except for the south-west coastal basin with sediments probably 6,000–7,000 feet thick. There are three major basins of type (4), with thicknesses exceeding 10,000 feet, but one of them has only been recently discovered and is as yet almost unknown. The other two are the Desert Basin, with Devonian to Jurassic stratigraphy and thicknesses probably up to 14,000 feet, and the North-West Basin, with Permian to Tertiary strata, with a known maximum thickness of over 12,000 feet. These two basins are of a geosynclinal type. They are idiogeosynclines in Umbgrove's, or paralic basins in Tercier's terminology. The economic significance of these facts is briefly discussed. In both basins there is an abundance of potential reservoir, cover, and source rocks of oil.

INTRODUCTION.

Western Australia is the largest of the six States comprising the Australian Commonwealth. With an area of 975,920 square miles it occupies about one-third of the continent of Australia. Many of the sedimentary regions are as yet little explored and their boundaries ill-defined, but it may be estimated that about one-third of the State, approximately 325,000 square miles, is made up of sedimentary rocks of younger than Precambrian age. These sediments range in age from the Cambrian to the Pleistocene. In some parts of the country they form no more than a thin sheet on top of the Precambrian, in others large sedimentary basins exist with thicknesses of many thousands of feet.

An excellent summary of the stratigraphy of Western Australia, representing the state of knowledge round about 1937, was included in a paper by Clarke (1938). Very important to this day is also the earlier account by Gibb Maitland (1919).

Of the facts that have come to light since that time some have been published in papers in various periodicals, a few have been incorporated in the

* Excluding the Precambrian System.

stratigraphical part of a recent text-book for Western Australian students (Clarke, Prider and Teichert, 1944), and many are as yet unpublished.

The present paper is the result of a stock-taking of existing knowledge and many previously unpublished observations and conclusions will be found scattered throughout the text.

The stratigraphy of the Pre-Cambrian sediments of Western Australia is not included in this paper, because it has been adequately described in the publications already referred to.

Apologies are offered to the reader for the personal note, which is perhaps too apparent in many places in this paper. However, the time is not yet ripe for the compilation of a standard text on the subject and the paper emerges as the result of eight years of personal experience in Western Australia without which it could not of course have been written.

This paper is not a historical treatise and references to earlier papers are, therefore, not exhaustive. The approach to the description of the rocks is somewhat different for different periods. Thus Permian sections are described proceeding from north to south and Tertiary rocks in the reversed geographical order. It was thought best as far as possible to proceed from the better known to the less known sections and from the more important to the less important areas.

A general summary of the stratigraphy of Western Australia is presented on the large stratigraphical table accompanying the present paper.

Throughout the text frequent references will be found to deep bores. It should be noted that few of these are diamond drill bores and even then cores are not always available. Either no cores were kept or the cores are not easily accessible at the present moment. Most deep bores in Western Australia are percussion bores from which no samples are available. The only sources of information are the original drillers' logs which are rarely satisfactory from the geologist's point of view. The logs of many early bores may be found in the "Report of the Interstate Conference on Artesian Water", Sydney, 1912, pp. 130–158; others were obtained by courtesy of the Geological Survey and of the Public Works Department, Perth. Unless otherwise stated all geological deductions regarding bore sections are based on such logs.

This paper was written when I was on the staff of the University of Western Australia and the manuscript was completed at the end of 1945.

CAMBRIAN.[1]

Distribution.

Rocks of proved Cambrian age are only known from the extreme north-east of the State, where they form the western end of a belt of Cambrian rocks that may extend intermittently right across the Northern Territory into western Queensland. On Western Australian territory the Cambrian rocks extend as a narrow belt along the boundary between approximately 18° 30′ and 16° 15′ S. lat., reaching westward from the boundary for 15 to 75 miles.

This entire area is covered by a sheet of basalt, about 2,000 feet thick, which has an irregular surface forming ridges and depressions. In the depressions

[1] The areas now known to be underlain by rocks of Lower and Middle Cambrian age were shown as "Carboniferous" on earlier maps up to about 1923. Subsequently they were mapped as "Upper Cambrian" by Wade and sometimes they were regarded as Middle Cambrian. On the other hand some maps published after 1923 show large areas of "Lower Cambrian" in the East Kimberley which include unfossiliferous quartzites and sandstones underlying Lower Cambrian basalts and are therefore undoubtedly of Pre-Cambrian age.

sedimentary strata which once covered the basalt everywhere have been preserved. These sediment-filled depressions have now generally been eroded down to a level below that of the basalt rises and are known locally as " Downs " country. The margins of these depressions are sometimes steep monoclinal flexures and the basal limestones of the sedimentary series occupy in many places a steeply dipping, sometimes vertical position. Since they are more resistant to erosion than both the overlying shales and the underlying top layers of the

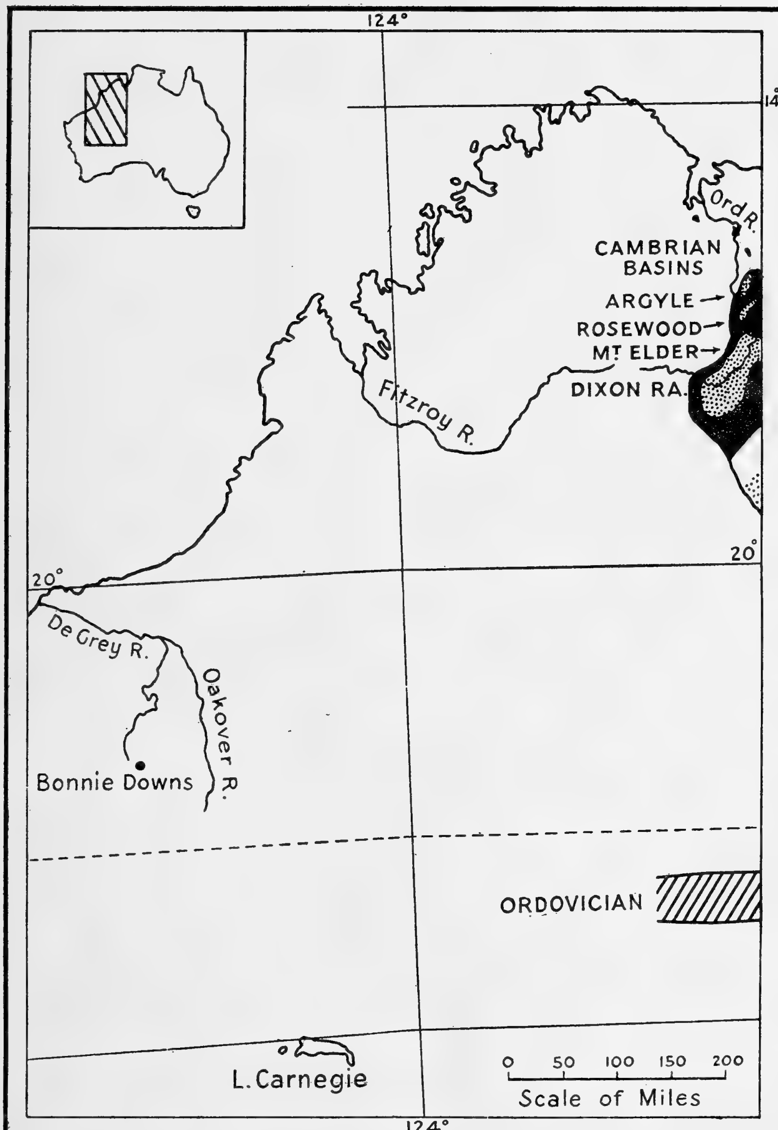

Fig. 1.—Distribution of Cambrian and Ordovician rocks. Black: basalt; stippled: sediments; oblique ruling: Ordovician. Bonnie Downs and Lake Carnegie are localities from which doubtful fossil remains of early Palæozoic age have been reported.

basalt (which are mostly agglomerates and vesicular flows) they form in many places almost vertical " limestone walls ", sometimes thirty to fifty feet high. These striking physiographical features have puzzled many earlier observers.

The main structural features in the arrangement of the Cambrian sediments are from north to south:

(1) Argyle Basin, about 25 miles long and seven miles wide, with the long axis striking N.E.-S.W., and faulted along its N.W. side against Pre-Cambrian and other rocks.

(2) Rosewood Basin, about 40 miles long and 11 miles wide, roughly parallel to the former.

(3) Hardman Basin, 75 miles long and 35 miles wide, which is subdivided by the Kelly Creek anticline into a smaller basin in the north (Mt. Elder basin) and a larger basin in the south (Dixon Range basin). This basin is truncated near its south-western end by a major fault zone, the Hardman fault.

The stratigraphy is most complete in the Hardman Basin, which will therefore be considered first. Only a small thickness of strata is preserved in the north-eastern part of the Rosewood basin (the only part so far investigated) and the succession in the Argyle basin is somewhat different from that in the more southern area.

It is possible that Cambrian or other Lower Palæozoic rocks will be found to occur on the Western Australian Plateau, where they may be associated with the Pre-Cambrian Nullagine series. West of Lake Carnegie (about 23° 20′ S. lat., 122° 20′ E. long.), an obscure impression of an edrioasteroid has been reported by Chapman from limestones interbedded with shales and sandstones, believed to be of Nullagine age.

Also, in 1944, fragmentary impressions of a gastropod and a merostome crustacean were found on Bonnie Downs Station, in sandstone mapped as Nullagine, about 35 miles south of Nullagine, and about 275 miles N.W. of the aforementioned locality.

Succession.

The Cambrian sequence consists of basalt flows and agglomerates at the base, overlain by sediments of Lower and Middle Cambrian, and perhaps Upper Cambrian age. The general succession is as follows (Teichert and Matheson, 1947).

Middle Cambrian.	*Mt. Elder series:* Red shales, overlain by brick-red sandstones, cross-bedded towards the top. Thickness, (approx.), 2,000 feet.
Lower Cambrian.	*Negri series:* Shales and limestones. Thickness, 850–1,000 feet.
	Basalt. Thickness, about 2,000 feet.

The basalts rest unconformably on Pre-Cambrian rocks. As described by Edwards (Edwards and Clarke, 1940), they range from olivine- to quartz-basalts and are of the tholeiitic or plateau-basalt type.

Throughout most of the area the base of the overlying Negri series is formed by a massive, hard limestone which is up to 50 feet thick (Plate IV, Fig. 1).

This is followed by alternating shales and limestones and the generalized section of the Negri series is as follows:

Negri Series.

	Feet.
Limestone	10
Calcareous shale	235
Limestone with *Girvanella*	10–20
Calcareous shales	Abt. 120
Limestone, lower part cherty, upper part pure, with *Redlichia forresti*	55
Calcareous shales	150–525
Basal limestone (cherty)	40–50

The four limestone beds of this series are usually well defined in the field. On the Western Australian side of the boundary the uppermost and the lowermost limestones are always unfossiliferous, but a few miles beyond the boundary, at Mt. Panton in the Northern Territory, the uppermost shales and limestones are fossiliferous and the section is here as follows:

Negri Series at Mt. Panton.

	Feet.
Limestone with *Girvanella* and *Biconulites* ..	10
Alternating shales and limestones with *Redlichia* and *Xystridura*, very fossiliferous	125
Limestone with *Girvanella* and *Biconulites* ..	10
Red and grey shales	135

Mt. Panton rises from a plain which is partly underlain by limestones which seem to correspond to the limestones with *Redlichia forresti* of Western Australia. The higher shales and limestones with *Xystridura* and *Redlichia* correspond to unfossiliferous shales and limestones on the Western Australian side of the boundary. *Xystridura* is a trilobite previously described from Queensland, where it is almost restricted to the *Dinesus* zone of the upper Templeton series of Middle Cambrian age, but in the Mt. Panton section the genus is associated with one or two large new species of *Redlichia* so that the beds must be classified as Lower Cambrian.

The faunal succession of the Lower Cambrian Negri series of Western Australia and the adjacent Northern Territory is therefore as follows:

Upper subzone with *Girvanella*.
Subzone with *Xystridura* and *Redlichia*.
Lower subzone with *Girvanella*.
Subzone with *Redlichia forresti*.

In the Argyle basin, near the northern end of the Cambrian belt, the succession of strata in the Negri series is somewhat different. The basal limestone is missing and the basalt is overlain by shales which may be as much as 1,000 feet thick. These are followed by a series of alternating limestones and shales which, however, contain only one fossiliferous horizon with *Girvanella*, *Biconulites*, and a small species of *Redlichia*. Other limestone beds are unfossiliferous. From its position in the section it appears that the *Girvanella* limestone of the Argyle basin has probably to be correlated with the lower *Girvanella* limestone of the southern area and is thus stratigraphically below the *Xystridura-Redlichia* subzone.

The Mt. Elder series is as yet incompletely known. In the vicinity of Mt. Elder it consists of 650 feet of basal red shales, overlain by about 1,300 feet of sandstones with a characteristic brick-red colour. Throughout most of their thickness these sandstones are well bedded, but the uppermost 100 feet or so are cross-bedded and towards the top the red colour gradually changes into pink and finally white. There is probably a greater thickness of this series west of the Ord River, particularly in the Dixon Range, and from the scanty information available it would seem that cross-bedded sandstones are here more prominent. It may be that the Mt. Elder series west of the Ord is thicker and that a greater part of the upper cross-bedded part is preserved there which is mostly eroded away in the vicinity of Mt. Elder.

The Mt. Elder series is conformable with the Negri series and there is no sudden change in the character of the sediments. Since the highest beds of the Negri series are of late Lower Cambrian age, much of the Mt. Elder series must be Middle Cambrian, although sedimentation might have continued into the Upper Cambrian.

In widely distant places, such as Behn River, Negri River and Elvire River we observed that immediately below its junction with the Negri series the basalt is invariably vesicular and in places agglomeratic. These softer rocks would have been easily eroded, if the surface of the basalt had been exposed for some time and it must therefore be assumed that no appreciable time interval elapsed between the cessation of volcanic activity and the beginning of the formation of the Negri series. It is therefore reasonable to assume that the basalts are of early to middle Lower Cambrian age.

Soon after its formation the basalt must have been submerged below a moderately deep sea in which the shales and limestones of the Negri series were deposited. Gradually the sea became shallower, and sandstones were laid down. Cross-bedding in the upper part of the sandstone series indicates further shallowing of the sea, preceding the final drying up of the area some time in the late Middle or Upper Cambrian.

Ordovician.[2]

A number of low ranges (Walter James Range, Robert Range and others) near the State boundary at about 24° S. lat. consist of sandstones and quartzites which are possibly an extension of the Ordovician Larapintine series of the Amadeus Sunkland in central Australia (Ellis, 1937).

The rocks are folded, but their thickness is not known and no fossils have been found, so that the correlation with central Australian rocks rests on similarities of lithology only. How far these rocks extend into Western Australia and what area they may cover is at present unknown. If the present opinion as to the age of these beds is correct, a sedimentary series measuring several thousand feet in thickness may be expected to be present in that part of the State, for the Ordovician of central Australia is up to 6,000 feet thick.

Silurian.[3]

No Silurian rocks are known from Western Australia.

[2] The Nullagine series and related beds, now considered to be of Pre-Cambrian age, have sometimes been classified as Ordovician.

[3] In the past quartzites of the Stirling Range in the South-west Division were sometimes mapped as " Silurian ", but are now regarded as Precambrian. Metamorphic Precambrian rocks of the East Kimberley Division were once classified as " Cambro-Silurian " or " Silurian ", but this notion has been abandoned for the last thirty years or so.

DEVONIAN.

Distribution.

Devonian rocks are not known in Western Australia outside the Kimberley Division. Here they occur in two widely separate areas: (1) East Kimberley,[4] close to the Northern Territory boundary, north of 16° S. lat. At present strata of Devonian age are known between the Ord River and the Northern Territory boundary and between approximately 15° 30′ and 16° S. lat. The bulk of the Devonian rocks in this area occurs in a large basin-like structure which has its centre in the Burt Range and part of which at least is in the Northern Territory where it has not yet been investigated. A minor occurrence of Devonian rocks

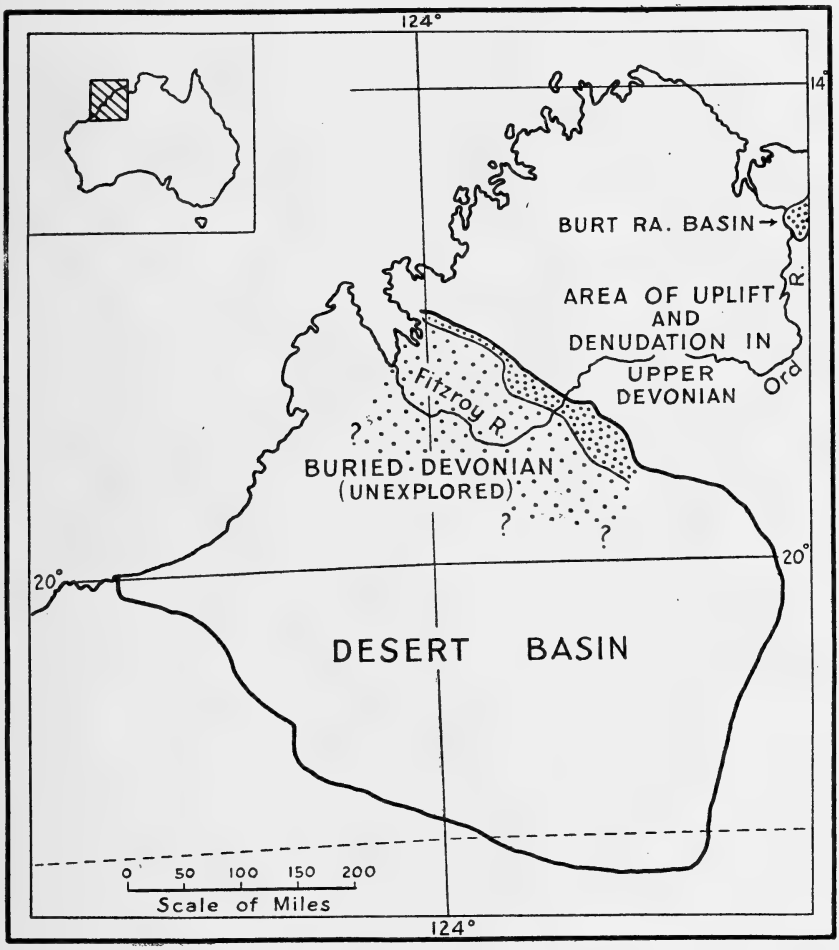

Fig. 2.—Distribution of Devonian rocks. Dense stippling: outcrop areas; wide stippling: buried Devonian.

[4] Many earlier maps of the East Kimberley Division, up to about 1924, show large areas of " Devonian " in country now known to consist of Precambrian and Palæozoic rocks and which incidentally also include some rocks of Devonian age. The same areas were shown on other, more recent maps, as " Lower Cambrian ", or as " Precambrian " without any new investigations having taken place. The first fossiliferous Devonian in the East Kimberley was discovered in 1941, but its full extent was not realized until 1945.

is known from the valley of the Ord a few miles below Ivanhoe Homestead. It is probable that further Devonian outcrop areas exist west of the Northern Territory boundary north of 15° 30′ S. lat., but this country is as yet geologically unexplored.

(2) West Kimberley, in a belt about 200 miles long and up to 40 miles wide, running from near the east side of King Sound (about 124° E. long., 17° S. lat.) south-eastwards to the vicinity of the Margaret River and Christmas Creek (about 126° 10′ E. long., 18° 35′ S. lat.). This belt includes a number of low limestone ranges such as Napier Range, Oscar Range, Geikie Range, Rough Range, Bugle Range. It widens towards the S.E., where it includes a good deal of flat and irregularly hilly country.

Succession.

(1) *East Kimberley* (Teichert and Matheson, 1947).

The chief development of the Devonian in this part of the country is in the synclinal basin whose centre is occupied by the Burt Range and which for the present may be called Burt Range Basin (Plate IV, Fig. 2). This series begins here with a thick series of conglomerates and sandstones which pass upward into shales, calcareous sandstones, and limestones which in turn are followed by another sandstone series. These rocks occupy the flat or slightly hilly country for several miles west of the Burt Range as well as the first, or westernmost ridge of the Burt Range itself. The succession is here as follows :

	Feet.
Upper sandstone series	1,000
Limestone series with interbedded shales and calcareous sandstones	4,000
Cockatoo sandstones and conglomerates ..	4,800
Total thickness	9,800

The Cockatoo sandstones and conglomerates rest on basalt which in one place was seen to be about 100 feet thick. The basalt in turn lies unconformably on Pre-Cambrian quartzites. It is at present impossible to state whether or not this basalt is contemporaneous with the Lower Cambrian basalt of the Argyle basin and the other Cambrian basins further south. Present indications are that in spite of its great similarity to the Cambrian basalt it may well be of Devonian age.

The Cockatoo sandstone series[5] itself begins with sandstones with interbedded conglomerates which contain quartzite pebbles. The sandstones are usually strongly cross-bedded ; many of them are only loosely cemented and quite soft, and they tend to weather out in pinnacles and pedestal rocks ; their colour is mostly grey, but red sandstones occur among them. In general it is the lower part, approximately the lower 1,500 feet or so, which is more resistant to erosion and weathering. Conglomerates gradually disappear in the sequence and the coarse-grained sandstones give way to fine-grained sandstones which are sometimes cross-bedded and usually very loosely cemented. Outcrops in this upper part of the Cockatoo series are therefore generally very poor. Mt. Cecil, however, on the western flank of the basin, only a few miles from the Ivanhoe-Argyle road, is a dome structure formed of higher sandstones of the Cockatoo

[5] The name is derived from Cockatoo Spring on the road from Ivanhoe to Argyle Homesteads, 26 miles from Ivanhoe. In this vicinity the weathering of the Devonian sandstone results in the formation of very sandy soil and this stretch of country is locally known as " Cockatoo sands ". These sandstones were first noted by Wade in 1924, who referred them tentatively to the Upper Carboniferous.

series in which imprints of *Lepidodendron* were found. The Mt. Cecil dome is traversed by a number of minor faults and silicification along the fault planes has provided a rigid lattice work around and between which the softer sandstones have been protected from erosion.

The Cockatoo sandstones pass gradually into the next following series, which is characterized by an alternation of sandstones, shales and an increasing number of limestone horizons. The lowermost limestones, interbedded with calcareous, fine-grained sandstones, are unfossiliferous, but several hundred feet higher up brachiopods begin to appear and the limestones become increasingly fossiliferous. Very little collecting has so far been done, but the general impression derived in the field was that species of *Camarotoechia* and *Meristella* appear first. They are soon joined by small species of *Productella* and some limestone horizons were found with characteristic *Camarotoechia-Productella* assemblages identical with those of the *Productella* limestone of the West Kimberley Division to be described below. Still higher up in the sequence new and larger species of *Productella* appear, accompanied by Spiriferids, *Straparollus*-like gastropods, by nautiloids of the *Spyroceras*-type, and by a rich fauna of smaller brachiopods, as yet unidentified. Not only the limestone beds themselves, rarely more than five or six feet thick, but also the intercalated calcareous shales and sandstones are in places richly fossiliferous.

Towards the top of the limestone series, the intercalated sandstones become more coarse-grained and the larger productids disappear from the limestone assemblages leaving only smaller brachiopods among which *Camarotoechia* is always prominent. Thus, the passage to the Upper Sandstone series is very gradual. This series is fairly uniform throughout, well-bedded, often with cross-bedding between the major bedding planes. A conspicuous feature are the many vertical burrows which are found in numerous horizons. They vary greatly in size although the burrows in one and the same beds are always of the same order of magnitude. Larger burrows may measure about two inches in diameter and may be up to 10 inches long. They are usually easily recognizable by the darker staining of the sandstone material filling them. Tracks, probably worm tracks, were seen on some bedding places, though they do not seem to be common.

At present I am inclined to consider the entire series of rocks described above as Upper Devonian. The lower part of the limestone series seems to correspond to the *Productella* limestone of the West Kimberley which has been correlated with Stage IV of the Upper Devonian standard section. The upper part of the limestone series is thus younger, most likely corresponding to Upper Devonian Stage V and the Upper Sandstone series then belongs to the closing stage of the Devonian period. The Cockatoo series must probably be correlated with the earlier Upper Devonian (Goniatite beds) of the West Kimberley Division. The end of the Middle Devonian was a time of uplift in an area east and north-east of the Fitzroy basin, probably mainly in the vicinity of the present Hall's Creek. Thick conglomerates and sandstones were deposited in the eastern part of the West Kimberley Division during early Upper Devonian time and it seems reasonable to assume that the Cockatoo sandstone series represents the detritus which was transported simultaneously northward from this uplift area.

The upper boundary of the Devonian in the Burt Range is as yet undefined as the actual contact with the overlying Carboniferous limestones has not been seen.

(2) *West Kimberley.*

Although no detailed mapping of the Devonian outcrops in this area has as yet been done, the chief outlines of the stratigraphy can be stated with some degree of reliability. The belt of Devonian rocks as shown on existing maps

of the State seems to take its beginning on the east side of King Sound, just north of the mouth of the Meda River. From here it strikes first eastward and then bends into a south-eastern direction. No details about this part of the outcrop area seem to be known and no geological features are discernible in this country from the air.

It is only a few miles north-west of the Alexandra River that the Devonian belt begins to form a distinct topographical feature : rough, weathered limestone outcrops begin to appear which, south-east of the Alexandra, become more prominent and form a low, very rugged limestone ridge known as Napier Range. Farther to the south-east follow ranges of a very similar lithological type : the Oscar Range and the Geikie Range. All along this belt the Devonian limestones are topographically very distinct. They overlie the Pre-Cambrian metamorphics to the north-east and they dip south-westward below the Permian. South-east of Geikie Range the Devonian belt widens and includes ranges, isolated hills and level country : Needle Eye Rocks, Mount Pierre, Fossil Hill, Rough Range, Bugle Range, and others. This belt is dissected by the Margaret River and Mount Pierre Creek and extends south-eastward as far as the Louisa River.

A great variety of facies is found among the Devonian rocks of this belt and the rock types range from conglomerates with boulders many feet in diameter on the one hand to pure reef limestones on the other. No lower Devonian is present, but both Middle and Upper Devonian are well represented (Teichert, 1943).

The lithology of the Middle Devonian is very uniform over the entire area. The rocks are almost exclusively limestone with only a few feet of grit and sandstone where the overlap on to the basal Pre-Cambrian rocks can be seen. In some places in the Rough Range beds of limestone containing angular fairly fresh fragments of felspar were seen a short distance above the base of the sedimentary series. For the time being the Middle Devonian limestones have been divided into two sections : a lower *Amphipora* limestone, and an upper *Atrypa* limestone. The Middle Devonian begins locally with unfossiliferous limestones, but in places *Amphipora* limestones rest directly on the Pre-Cambrian basement. This part of the sequence is very monotonous, *Amphipora ramosa*, a small branching stromatoporoid, filling the limestones in untold numbers. Although *Amphipora* biostromes make up the section of a considerable vertical extent, other fossiliferous layers are occasionally intercalated. Some of them may be described as *Thamnopora* biostromes, others as *Stachyodes* biostromes, and so forth. Certain other species, notably *Prismatophyllum* and the gastropod *Murchisonia* are restricted to certain layers without, however, forming definite biostromes.

Higher up in the section the biostrome facies is replaced by typical bioherms. Small reefs of concentrically built stromatoporoids of the *Actinostroma* type begin to appear and at the same time shelly fossils become more numerous. Since *Atrypa* is an ubiquitous member of the faunas of these higher Middle Devonian limestones, the name *Atrypa* limestone has been given to this part of the section.

The thickness of the Middle Devonian has only been measured in one or two places where it is in the vicinity of 2,000 feet. In the north-western limestone belt (Napier and Oscar Ranges) the entire Devonian is represented by a uniform limestone series and Middle and Upper Devonian have not yet been sharply distinguished everywhere. In general the Middle Devonian limestones seems to become more fossiliferous towards the south-east, and in the Rough Range, near Mount Pierre Creek, and in the ranges and on the plains in that general neighbourhood the *Atrypa* limestone is in places very fossiliferous and contains a great variety of brachiopods which include *Leptaena*, *Rhipidomella*, *Schizophoria*, *Spirifer*, *Ambocoelia*, *Camarotoechia*, *Uncinulus*, *Hypothyridina* and *Pugnax*.

In addition pelecypods, gastropods, and cephalopods may occur. In the bioherm facies corals are often found mixed with the prevailing stromatoporoids.

In the Upper Devonian the diversity of facies is very much greater. As has already been said, in the Napier-Oscar-Geikie Range belt both Upper and Middle Devonian are represented by limestones, the Upper Devonian being characterized by a preponderance of reef limestones. In this part of the sequence individual stromatoporoid reefs attain considerable dimensions and may measure up to 50 and 60 feet in height and several hundred feet in length, but hardly ever are any other fossils associated with them, with the exception of a few species of large pelecypods and gastropods which may occur in some horizons.

The top of this limestone series is formed by brachiopod limestones in which *Productella* and *Camarotoechia* are very abundant. The total thickness of the Middle and Upper Devonian limestone series does not seem to exceed 5,000 feet.

Of greater stratigraphical and lithological interest is the south-eastern area of Devonian rocks where an intricate pattern of interfingering facies is present, of which so far only the bare outlines are known.

Of considerable stratigraphical and palæographical importance is the goniatite facies which is now known to be distributed over considerable areas in the vicinity of Mt. Pierre as well as farther south in the south-eastern part of Rough Range and on the plains and in the hills between Rough Range and the upper course of Mount Pierre Creek towards Mt. Pierre Well. These rocks are mostly red and grey calcareous sandstones and shales (typical " red bed " facies) in which goniatites occur in many places in great abundance. Other fossils, particularly sponges, corals and brachiopods, are by no means absent, and along certain belts small stromatoporoid reefs are intercalated. In other places these beds grade into pure brachiopod shales or into shales with calcareous fossiliferous concretions.

Towards the east the beds become increasingly conglomeratic (Plate IV, Fig. 3) and the hills between the Trigonometrical Stations J 8 and J 7 are thickly covered with layers of residual boulders of these conglomerates (Plate V, Fig. 1). From the air it can be seen that these beds extend east as far as the Louisa River.

Thanks to the abundance of good index fossils in the red bed facies and locally also in the conglomerates the task of their correlation was not particularly difficult and until it is possible to map individual rock units in greater detail the strata have been divided in a general way into four stages which correspond rather closely to the first four Upper Devonian stages (I-IV) of the Upper Devonian goniatite type section of Germany.

The earliest of those, Stage I, is characterized by the goniatite *Manticoceras*. It became first known from Bugle Gap (Teichert, 1941*b*) where red beds with *Manticoceras* and *Beloceras* overlap Middle Devonian reef limestones. Associated with the goniatites are other fossils, including a unique trilobite fauna with *Cyrtosymbole*, *Pteroparia*, *Drevermannia*, *Chaunoproetus*, *Harpes* and *Scutellum*.

The *Manticoceras* beds have only been studied in the field in a few places. Elsewhere they are represented by shales with calcareous concretions containing *Manticoceras*, *Koenenites* and *Timanites*, pointing to a very slightly younger age than the red bed fauna mentioned above.

Higher than the *Manticoceras* beds is a red bed series with a somewhat poorer fauna of goniatites among which *Cheiloceras*, *Tornoceras* and *Dimeroceras* are most prominent, non-cephalopod species being all but absent. At present this *Cheiloceras* fauna is known from the vicinity of Mount Pierre, from south-eastern Rough Range, and from the hills to the south-east of the latter. Towards the east the calcareous sandstone facies grades into conglomerates interbedded with red sandstones, some of which contain goniatites.

The next higher series is characterized by the goniatite *Sporadoceras*. The associated faunas are very much richer and more varied than those of the

preceding stratigraphical stages. In addition to goniatites which include *Tornoceras*, *Dimeroceras* and *Pseudoclymenia*, and nautiloids (including *Wadeoceras*) there is a fair variety of brachiopods (*Rhipidomella*, *Spirifer*, *Pugnax*, *Productella*, *Meristella*, *Ambocoelia*, *Gypidula*, *Camarotoechia* and others) and some corals and sponges. Locally small stromatoporoid reefs, often associated with a characteristic fauna of cephalopods, appear in these beds (Plate IV, Fig. 4).

As in the case of the *Cheiloceras* beds the typical red bed facies of the *Sporadoceras* beds passes south-eastwards into coarse-grained sandstones and

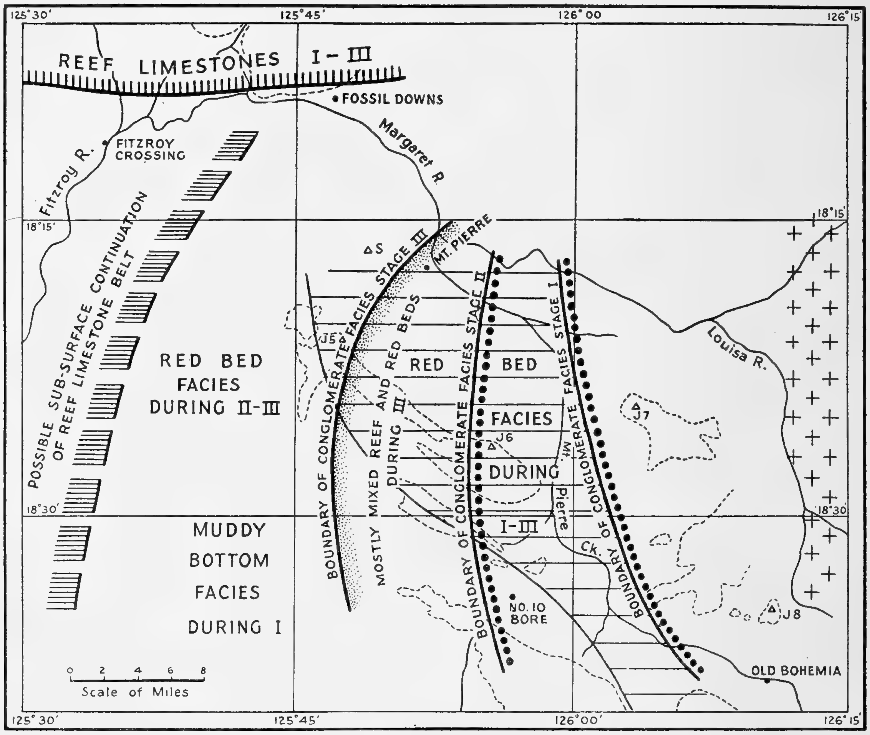

Fig. 3.—Facies map of the Upper Devonian of the Margaret River-Mount Pierre Creek area, West Kimberley Division.

conglomerates. The whole sequence of rocks is regarded as an equivalent of Upper Devonian Stage III of the German type section. Its thickness as far as known at present does not seem to exceed a few hundred feet.

The last member of the Upper Devonian is a limestone series up to about 200 feet thick which contains abundant brachiopods and has been termed *Productella* limestone. In addition to *Productella* it contains many other brachiopods. Most abundant is *Camarotoechia*. The two genera together are sometimes rock-building. Other common brachiopods belong to *Schizophoria*, *Leptostrophia*, *Stropheodonta*, *Athyris*, *Meristella* and *Pugnax*. Goniatites are absent from this limestone, but some interesting clymenoids occur which seem to be related to *Platyclymenia*, *Cyrtoclymenia* and *Laevigites*. The appearance of clymenoids in these beds suggests correlation of the *Productella* limestone with Upper Devonian Stage IV of Germany. The *Productella* limestone seems to be rather uniformly developed over the entire area. Small stromatoporoid reefs are scattered through it everywhere, but no major reefs were built during the

time of its deposition. It marks the closing stage of Devonian sedimentation of the West Kimberley. As has been mentioned above, younger Devonian strata corresponding to the higher Devonian beds elsewhere, are known from the East Kimberley Division close to the Northern Territory boundary.

Devonian Palæogeography of West Kimberley.[5a]

"Sedimentation began some time in the Middle Devonian probably in late Eifelian or early Givetian time; the sea transgressed over the Pre-Cambrian in a general easterly direction. The basement must have subsided at a rapid rate and the Pre-Middle Devonian relief of the land on the whole must have been low, for there was little deposition of clastic material and very soon the formation of limestone commenced in the entire area." Thick limestone series were deposited largely by the activity of the small branching stromatoporoid *Amphipora ramosa.* Other stromatoporoids appear somewhat later in the Middle Devonian and from then on contribute materially to the limestones of the Middle and Upper Devonian in the north-western area of distribution of Devonian rocks. Later in the Middle Devonian *Amphipora* disappeared completely from the entire area and richly fossiliferous brachiopod limestones were deposited. The coast at this time must have been far to the east of the present area of distribution of Middle Devonian rocks, for few indications of a Middle Devonian littoral facies have as yet been found.

"A profound and very sudden change of conditions took place between the Middle and Upper Devonian. There must have been a sudden uplift of the mainland in the east which also affected the eastern reef belt of late Middle Devonian age, and which caused a retreat of the sea in a westerly direction. Reef-building activity ceased and massive conglomerates of Pre-Cambrian rocks were piled up on top of the Middle Devonian reefs." The conglomerates are found, in many places only as residual concentrates of quartzite boulders, in the country between Louisa River and Mount Pierre Creek in the vicinity of Trigonometrical Stations J 7 and J 8, where they rest on Middle Devonian reef limestones. To the west the conglomerates pass into a sandy and shaly facies though conglomerates are still present as far as the south-eastern part of Rough Range.

The area west of about 123° 40′ E. long. remains essentially unaffected by these changes. As mentioned before all along the limestone belt of Napier, Oscar and Geikie Ranges reef-building activities, mainly of stromatoporoids, continued without a major break from the Middle into the Upper Devonian. Between this "barrier reef" and the coast in the east there existed a wide lagoon which was gradually being filled in by clastic sediments during Upper Devonian time.[6]

The geological events that led to the profound changes in sedimentation in the south-east must have occurred suddenly at the beginning of Upper Devonian Stage I, for even during substage Iα they were already in operation and more stable conditions had been re-established. During the time of Stages I, II and III (*Manticoceras*, *Cheiloceras* and *Sproradoceras* beds) the land in the east

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[5a] In this chapter all passages in " " are quotations from a similar chapter in Teichert (1943)

[6] Wade's "Gogo series", tentatively referred by that author to the Carboniferous, is the sandy facies of this Upper Devonian area of sedimentation. *Manticoceras*, *Koenenites* and other Upper Devonian goniatites were found around No. 10 Bore on Gogo Station and in other areas shown as Gogo series on Wade's map. His "J 8 beds", interpreted as Permian moraines, are the contemporaneous conglomeratic facies. *Cheiloceras* was found in pockets in such conglomerates in low hills south-east of the Rough Range, and in the south-eastern part of the Rough Range similar conglomerates were found interbedded with sandstones of Stage III of the Upper Devonian. (See A. Wade, *Geological Map of the Kimberley Division of Western Australia*, Canberra, 1937.)

must have continued to rise slowly, because it furnished a constant flow of clastic material which was transported westward into the sea.

" Details of the history of the area during Stage I are as yet hard to decipher, but during the later part of Stage II conglomeratic material was being transported much farther west than at the beginning of I. Between these conglomerates in the east and the barrier reef in the north-west there was a zone, at least 10 miles wide, probably with sandy bottom in the east and more calcareous muddy bottom in the west where a fauna existed which was composed almost exclusively of goniatites and a few nautiloids." This may have been an almost completely enclosed basin with badly aerated bottom water which was unfavourable to benthonic life, but where nekto-benthonic cephalopods were able to exist.

During the time of Stage III (*Sporadoceras* beds) clastic material was transported still farther west than before, as is clearly indicated by the conditions in the south-eastern part of Rough Range. Here sandy *Cheiloceras* beds are overlain by Lower *Sporadoceras* limestones with intercalated sandstones and conglomerates and the Upper *Sporadoceras* beds in this section seem to be predominantly sandy and conglomeratic. Still farther west the Lower *Sporadoceras* beds are represented by a bioherm facies and sandstones and shales predominate in the Upper *Sporadoceras* beds.

" Living conditions must have been much improved for a rich fauna now invaded the lagoon. Close to the barrier reef in the west conditions showed little change from the immediately preceding stages and goniatites dominated the scene, although there was gradually increasing migration of other forms of life, mainly corals and brachiopods, into this zone." Farther inshore a belt of minor stromatoporoid reefs is distinguishable between the clastic facies in the east and the goniatite red beds in the west. Remnants of this belt are now exposed in south-eastern Rough Range and at Mount Pierre.

It seems that " the clastic sediments described above were deposited in a large delta formation and that the bulk of the material was transported in a westerly direction from an area somewhere north of Trigonometrical Station J 8 " and probably east of the Louisa River. The barrier reef belt in the west may be expected to have continued south of the area in which the present outcrops of reef limestones are found. One may expect to find them under a thick cover of Permian sediments at least as far south as St. George's Range and the lower course of Christmas Creek, although the exact nature of the Devonian rocks below the Permian farther towards the centre of the Desert Basin could only be determined by borings.

Had conditions remained unchanged the lagoon between the barrier reef and the coast would eventually have been filled by clastic sediments. As it was, however, the entire area subsided after the deposition of the *Sporadoceras* beds, the coast receded eastward and uniform conditions reminiscent of those of the Middle Devonian were restored over the entire area. Limestones and limestone conglomerates (*Productella* limestone) were deposited, reef-building activity was reduced to a small scale, and a rich fauna, mainly of brachiopods, moved in. This subsidence also affected the outer barrier where the reefs were brought so far below sea-level that they died.

CARBONIFEROUS.[7]

Distribution.

At present only known from the Burt Range in the East Kimberley Division, about 15° 50′ S. lat., close to the Northern Territory boundary (Plate V, Fig. 2).

[7] At one time or another all Palæozoic rocks of Western Australia have been mapped as Carboniferous and many maps have been published up to fairly recent times that show a greater or lesser extent of Carboniferous strata in various parts of the State. All these areas have eventually turned out to be either Cambrian, Devonian, or Permian. The first Carboniferous in Western Australia was discovered by R. S. Matheson and myself in 1945.

Succession.

Strata of this age are as yet very poorly known and at present only 350 feet of Bryozoa limestone can be referred to the Carboniferous with certainty. This limestone overlies the uppermost Devonian sandstones, though the contact between the two series has not yet been observed. The limestone is hard and dense and extremely fossiliferous. In addition to Bryozoa it contains some corals as well as brachiopods, but very little collecting has been done so far. The fossils include *Rhipidomella australis*, *Orthothetes*, *Camarotoechia*, *Dielasma*, as well as spiriferids and productids.

PERMIAN.[8]

Distribution.

Permian rocks are well exposed in Western Australia in a number of important areas (Teichert, 1941*a*). In order of size and importance these are: (1) Desert Basin in the Kimberley and Eastern Divisions. This is an area of unknown extent, possibly as much as 140,000 square miles, of which, however, not more than 20,000 square miles have been geologically examined. (2) The North-West Basin in the North-West Division, where an area of about 15,000 square miles extending from the vicinity of the Murchison River in the south to somewhat north of the Lyndon River in the north is underlain by Permian rocks. This is about 300 miles long and up to 60 miles wide. (3) Various outcrop areas east of Geraldton and in the vicinity of Mingenew and the Irwin River, at the northern end of the South-West Coastal Plain between approximately 28° 30′ and 29° 20′ S. lat. (4) The Collie-Wilga coal basin in the south-west (about 31½° S. lat.). (5) A recently discovered and as yet very insufficiently known area in the East Kimberley Division, near the Northern Territory boundary in the vicinity of 16° S. lat.

A large area in the Central Division is covered by boulder beds and sandstones of uncertain age, known as Wilkinson Range series. These will here be described in the chapter on the Cretaceous, although they might conceivably be Permian as advocated by some authors. Proof of their Permian age would of course greatly change our ideas of the Permian palæogeography of the interior of Western Australia.

Succession.

(1) *Desert Basin.*

The greater part of the Desert Basin is geologically unexplored, but near its northern margin the stratigraphy has been studied in some detail. This part of the basin is traversed by the Fitzroy River and its tributaries, which is the only major surface drainage system in the basin. The remaining 120,000 square miles are for all practical purposes *terra incognita*. The southern margin of the basin has been visited by geologists in a few places and two geologists have traversed the eastern half of the Basin along the Canning Stock Route, but no attempt at a systematic survey of any part of this area has ever been made. The following account will, therefore, almost exclusively deal with the stratigraphy of the Fitzroy River area (Plate V, Fig. 3).

[8] Rocks of Permian age in Western Australia were at first regarded as Carboniferous. Since about 1910 it became more and more customary to refer to them as "Permo-Carboniferous" the implication being that the lower part of the system was Upper Carboniferous, the higher part Permian. In 1931 Sir Edgeworth David proposed the name Kamilaroi System for the "Permo-Carboniferous" of eastern Australia. This term has never been widely used in Western Australia and in more recent years the Permian affinities of all the Western Australia faunas concerned have been recognized.

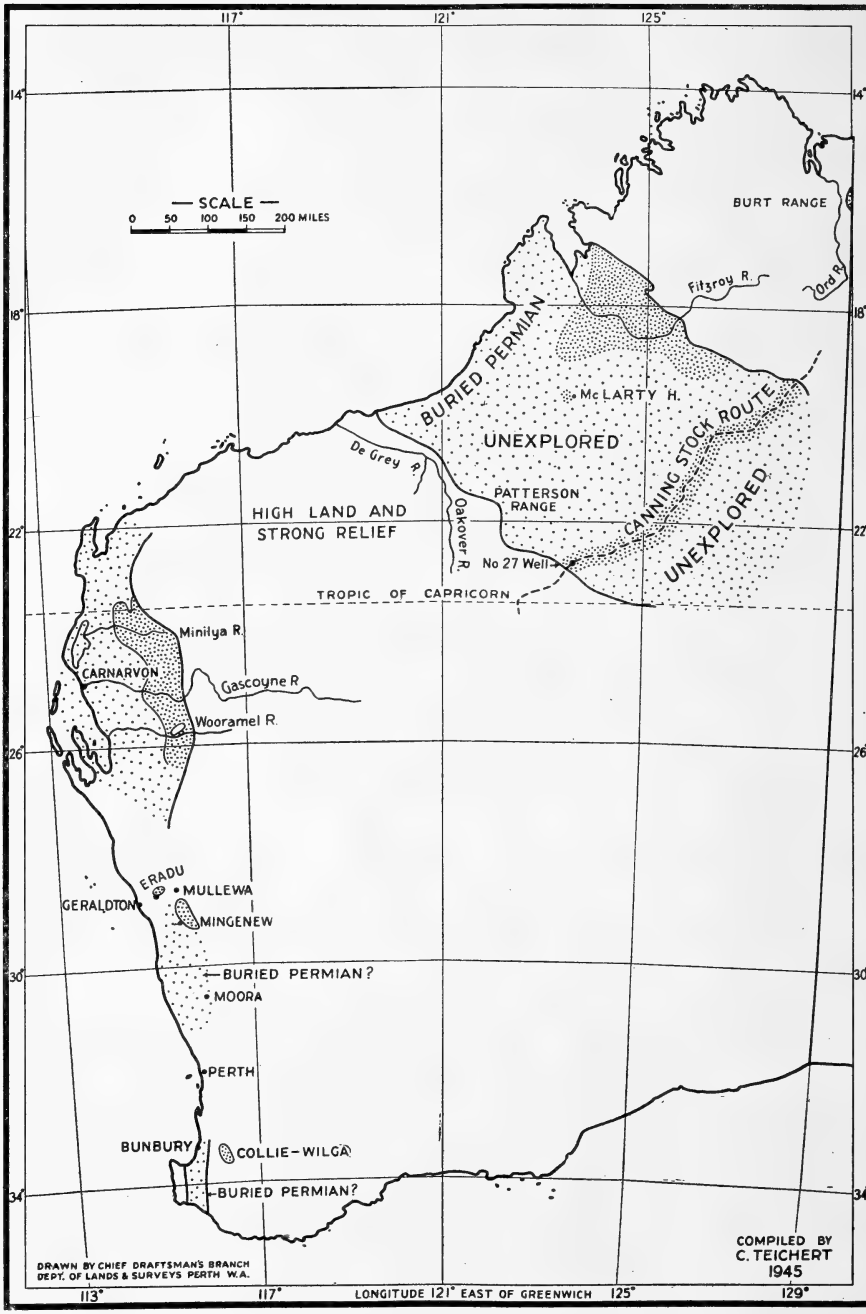

Fig. 4.—Distribution of Permian rocks. Dense stippling : outcrop area ; wide stippling : buried Permian.

A somewhat generalized table of the Permian sequence in this area is as follows (according to Wade):

	Feet.
Erskine series. Estuarine conglomerates, grits, sandstones, and shales with plants	350
Upper Ferruginous Series. Clays, grits, sandstones, mostly limonitized, with rich marine fauna	1,400
Nooncanbah Series. Clays, shales, with calcareous horizons, many of them passing into sandstone. Rich marine fauna	1,200
Lower Ferruginous Series. Coarse, dark grits and conglomerates, sandy shales and flags, mostly heavily limonitized. Rich flora	2,000
Nura Nura Limestone. Grey, sandy limestone with fossiliferous erratic boulders, arenaceous shales	20
Grant Range Series. Sandstones, grits, arkoses, conglomerates, containing pebble bands, and in places larger boulders. Boulder clay and tillites. Clayey sandstones. Fossil wood	2,300
Kungangie Series of Christmas Creek area. Fine-grained sandstones and clayey sandstones, coarse red grits, sandy shales and cherts, probably also tillites and boulder clay. Fossil wood	2,000

In the Poole Range, south-west of Christmas Creek (18° 50′ S. lat., 125° 45′ E. long.), there is a fine series of boulder clays and tillite, known as Willanyie beds, which contain abundant ice-scratched, faceted, and polished boulders. This series may be over 1,000 feet thick, and it may be the equivalent of the Grant Range series which occurs principally along the main valley of the Fitzroy.

All these lower, clastic series seem to be very much alike and it would seem that their proper correlation in the various parts of the area has not yet been fully established. The Grant Range, Kungangie and Willanyie beds may all be contemporaneous.

There can, however, be little doubt as to the presence everywhere in this area of sediments of glacial origin, probably everywhere in excess of 1,000 feet, and possibly several thousand feet thick. It may be expected that the thickness of these lower beds is somewhat variable and it is, therefore, difficult to give a reliable estimate of the thickness of the entire Permian sequence. According to Wade it may be between 7,500 and 8,000 feet. A series of conglomerates east of the main area of distribution of the Permian rocks (" J 8 beds ", because they occur in the vicinity of Trigonometrical Station J 8), formerly believed to be of Permian age has turned out to be Upper Devonian.

The Nura Nura limestone is of great interest because it is the lowest horizon with marine fossils in this sequence. It is fairly fossiliferous (chiefly brachiopods and Bryozoa), though most fossils are as yet unidentified. Near the top there is a layer of limonitized fossils which include *Metalegoceras clarkei* and *Thallassoceras wadei*, indicating an age not younger than Artinskian.

The Lower Ferruginous series contains a flora of *Glossopteris*, *Vertebraria*, *Noeggerathiopsis*, *Lepidodendron* and *Bothrodendron*. It is lithologically very uniform throughout its entire thickness.

The Nooncanbah series is extremely fossiliferous. Bryozoa and brachiopods are the most prominent groups, although corals and crinoids are also repre-

sented. Among the brachiopods are large productids and spiriferids as well as many smaller genera (*Strophalosia*, *Cleiothyridina et al.*).

The Upper Ferruginous series (also known as Liveringa series) is essentially characterized by the presence of brachiopods and pelecypods which include species of *Streptorhynchus*, *Cleiothyridina*, *Aulosteges*, *Tæniothærus*, *Linoproductus*, *Waagenoconcha*, *Spirifer*, *Stutchburia*, *Cardiomorpha*, *Schizodus* and the Timor genus *Atomodesma*. The gastropods include large pleurotomarids, a large *Bellerophon*, and *Conularia*. Near the top of the series fusulinids (*Verbeekina* and *Neoschwagerina*) have been found. These seem to be the highest marine Permian beds in the Fitzroy River area.

The sandstones of the Erskine series are rich in plant fragments but poor in identifiable remains. *Lepidodendron*, *Cordaites* and *Phyllotheca* have been doubtfully determined from this series.

Whereas, as has been pointed out above, the intra-basin correlation of the lower, glacial, series is as yet somewhat unsatisfactory, due, of course, chiefly to the absence of fossils in these older beds, the sediments from the Lower Ferruginous series to and including the Erskine seem to be more evenly distributed over the entire area and there seem to be fewer changes in facies. However, no palæontological zoning has as yet been attempted in the marine section of the sequence and detailed correlation of many occurrences is, therefore, difficult.

The Permian rocks of the Fitzroy area are slightly folded, forming broad anticlines, domes and synclines. Towards the south they can be seen to continue into the Desert Basin, but the full extent of the outcrops in this direction has not yet been mapped.

In the western interior of the basin Permian fossils seem to occur in the vicinity of the McLarty Hills (123° 30′ E. long., 19° 40′ S. lat.) (Clapp, 1926).

A few observations are available from the south-western margin of the basin, where sandstones and grits are reported from the Paterson Range (22° S. lat., 122° 15′ E. long.). These have been regarded as Permian, although no fossil evidence is available. However, 100 miles to the south-east, at No. 27 Well on the Canning Stock Route, sandstones with undoubtedly Permian fossil have been found. This locality is only 10 miles from the south-eastern margin of the Desert Basin. From here the Canning Stock Route winds across the Desert Basin in a north-easterly direction for about 400 miles (Talbot, 1910 ; see also the brief account of L. J. Jones' traverse in Hobson, 1936, pp. 24-25). Along much of this route flat-lying sandstones have been observed but no fossils have been found.

About 75 miles north-west of the Paterson Range a tillite occurrence has been reported near Braeside Station. This may well be of Permian age. Near by sediments, mostly limestones, are known to occur in the valley of the Oakover River and although they have been mostly referred to younger periods, they may quite possibly be Palæozoic.

(2) *North-West Basin.*

Although no doubt Permian rocks underlie the entire North-west Basin, outcrops are restricted to an area of about 15,000 square miles, occupying approximately the eastern half of the surface of the basin. The extent and configuration of this area is now fairly well known, but detailed stratigraphical investigations have been made in very few spots only. In the past it has been attempted to apply one and the same stratigraphical nomenclature to the rocks in all parts of the basin, but as more details become available it will become obvious that considerable lateral changes in facies and thickness of the strata exist and a multiple stratigraphical terminology will ultimately have to be developed.

The best known section is at present that along and in the vicinity of the Minilya River (approx. 24° S. lat.),[9] where, however, the lower part of the sequence is as yet only incompletely known (Plate VI, Figs. 1, 2). The upper, more accurately determined part is the following :

Wandagee Hill series.[10] Coarse-grained sandstones, partly cross-bedded. Few fossils	700 feet
Wandagee series. Well-bedded fine to medium grained sandstones and shales. Very fossiliferous	2,350 feet
(*d*) " Linoproductus Stage." Fine to medium grained sandstones, in many places strongly ferruginous. 1,000 feet.	
(*c*) " Schizodus Stage." Well-bedded, shaly and friable sandstones, greenish grey to brown. Rich in fossils (pelecypods) in some places, almost unfossiliferous in others. 190 feet.	
(*b*) " Calceolispongia stage." Grey, fine to medium grained sandstones and grey and black shales. Very fossiliferous. 600 feet.	
(*a*) " Lingula stage." Carbonaceous and gypseous shales, with some sandstone and limestone horizons (the latter fossiliferous). 560 feet.	
Cundelgo series. Fine grained shaly to coarse grained massive sandstone, commonly cross-bedded, with many intercalations of shale. Fossils in some layers only	1,000 feet
Bulgadoo series. Grey to black carbonaceous shales, in places gypseous, with very few sandstone beds. Not very fossiliferous	2,200 feet

The total thickness of these rocks is 6,250 feet, but it is not known how far they are above the base of the Permian sequence ; it seems, however, likely that another 3,000 to 3,500 feet of sediments are present. The total thickness of the Permian in this section is therefore very probably in the vicinity of 10,000 feet.

From present information it seems that the thickness decreases as we go south. Raggatt found the following section in the vicinity of the Gascoyne River, 75 miles to the south (about 25° S. lat.) :

Kennedy series. Sandstones	700 feet
Byro series. Mudstones, shales, sandstones, sandy limestones	2,400 feet
Wooramel series. Medium grained white sandstones ..	Up to 180 feet
Callytharra series. Limestones and mudstones	Up to 460 feet
Lyons series. Limestones, sandstones, glacial conglomerates	Up to 2,400 feet
Total up to	6,140 feet

[9] Mostly known from unpublished observations by the writer in 1938, 1939, 1940 and 1941.

[10] Provisional name, introduced in C. Teichert, " Permian Crinoid Calceolispongia " (*Geol. Soc. Am., Mem.*, in press). At present the correlation of these sandstones towards the north and south is unkown.

The Callytharra series is represented in the Minilya River section by 675 feet of calcareous shales and limestones—a thickening of well over 200 feet as compared with the Gascoyne section (Plate V, Fig. 4). The Wooramel sandstone series has not been accurately measured in the Minilya section, but is certainly not less than 180 feet. No figures are at present available for the Lyons series in the Minilya area.

The country south of the Gascoyne River has only been superficially examined, but from data collected by Dee and Rudd it would seem that along the Wooramel River, 50 miles south of the Gascoyne, the thickness of the Permian might have decreased to something like 2,800 feet, although this might represent a very conservative estimate.

Apart from the great thickness of the beds in the northern part of the basin, the most noteworthy feature is that the sequence is entirely marine. Here we find the only wholly marine Permian sequence in Australia and without doubt *one of the thickest marine Permian sequences in the world.*

(3) *South-West Division.*

In the south-western part of the State there are a number of scattered areas of Permian rocks. Good outcrops of marine strata are found 30 to 40 miles from the coast of the Indian Ocean on the Irwin River near and east of Mingenew (29° 10′ S. lat.) as well as farther north and south (Plate V, Fig. 3).

Excellent sections are seen in the two branches of the Irwin River, known as North Irwin and South Irwin, where the sequence is as follows :

	Feet.
White sandstone and shales	200
Carbonaceous shales with ferruginous sandstone layers and erratic boulders	120
Coal Measures. Laminated and cross-bedded, plant bearing sandstones with several coal seams ..	140
Fossil Cliff limestone ; richly fossiliferous shale with limestone layers	190
Metalegoceras series. Mostly unfossiliferous shales with limestones and claystones	2,500
Tillites, calcareous grits and Fontainebleau sandstones	200
Total	3,350

As far as known at present the area covered by these sediments is not more than about 100 square miles. They are folded into a flat north-pitching anticline. However, fossiliferous sandstones occur in the immediate vicinity of Mingenew and it is quite possible that marine Permian rocks have a much wider distribution in that part of the country. No other areas of marine Permian are known in the South-West Division, but some non-marine sedimentary basins may be briefly mentioned. One of these is the *Eradu basin*, where conglomerate sandstones and shales with interbedded coal seams have been found to a depth of about 1,200 feet. (Blatchford, 1930.) The thickest coal seam is 22 feet thick, but unfortunately, like the Irwin River coal, the Eradu coal is of low heating quality (more in the nature of a brown coal). Nevertheless both coal fields are at present being tested for their economic possibilities.

From Eradu the sediments continue eastward below the surface for thirteen and a half miles farther east, in the direction of Mullewa, 1,360 feet of sandstone and shale were traversed by a bore, but no coal seams were found here. It is

possible that these beds extend more or less continuously farther to the east and south-east and that they link up with the outcrops of the Irwin River district.

The southern continuation of this belt of Permian strata is likewise a matter for speculation. A deep bore at Moora, more than 100 miles south of Mingenew, penetrated almost 1,100 feet of grits, sandstones, shales and a few limestone horizons, below the lowest bed with Jurassic plants (probably Lower Jurassic), and the suggestion that these beds represent the continuation of the Irwin River Permian seems altogether reasonable.

Nothing further is known of the Permian until the Collie coal field is reached (Limb and Kent, 1939), at present the only productive coal field of Western Australia. It is situated 100 miles south of Perth (about 33° 10′ S. lat.). Although the full extent of the basin is unknown, it is not less than 100 square miles. The succession consists of sandstone and shale with interbedded coal seams of an aggregate thickness of 130 feet. The total thickness of the sediments is unknown, but is probably not less than 2,000 feet.

A Permian age is proved by the abundant occurrence of *Glossopteris* and *Gangamopteris* in certain horizons. The area is well outside the Coastal Plain, situated on the Precambrian shield, and the sediments are downfaulted.

South-south-east of the Collie basin is the Wilga basin with at least 700 feet of sandstones and shales with coal seams which have not yet been commercially exploited. Additional minor basins might exist further south of which the Fly Brook basin may be an example.

Coal has also been struck in bores near Bunbury on the west coast and in the sedimentary area south of Bunbury between the Western Australian Plateau and the Cape Leeuwin-Naturaliste horst in the west, but it cannot be decided whether these little-known sediments are of the same age or younger.

(4) *East Kimberley Division* (*Burt Range Basin*). (*Teichert and Matheson*, 1947.)

Very little can be said about the section in this part of the country at the present moment. In the Burt Range, close to the Northern Territory boundary, a conglomerate of about 50 feet was seen to rest with a very slight unconformity on the Carboniferous Bryozoan limestone. The conglomerate is followed by about 70 feet of coarse-grained sandstone and by several hundred feet of still higher beds which we were unable to examine.

However, elsewhere in that vicinity thick conglomerates were found which were quite unlike any Cambrian, Devonian or Carboniferous rocks known from that district. These conglomerates seem to form a considerable portion of the southernmost part of the Burt Range and are separated from the Devono-Carboniferous section of the central Burt Range by a major fault. The conglomerate is here fully 500 feet thick. There is very little indication of bedding and no sorting at all. Pebbles and boulders of any size up to two feet diameter occur rather tightly packed together. The same rock forms a prominent hill a few miles to the south, about one mile north of Cockatoo Spring, where well over 500 feet must be exposed. Although no scratched or faceted pebbles were found, a glacial origin of the conglomerate is perhaps not impossible. Elsewhere in the East Kimberley similar conglomerates occur associated with red sandstones, as, e.g., on the east side of Mt. Misery, and the same conglomerate may also be distributed further inland, west of the Ord River, in the Conglomerate or Ragged Range. Blatchford's (Blatchford, 1928) description and pictures of the rocks of this range agree so closely with the conglomerates north of Cockatoo Spring and in southern Burt Range that there can be little doubt that they belong to the same series. It is also possible that a thick series of sandstones and white shales at Mt. Brooking and vicinity is of the same age, though this is at present hardly more than a suggestion.

Permian Correlation.

For a long time correlation of the Permian rocks of Western Australia has been difficult. At first they were regarded as Carboniferous. At a later stage they were, in common with contemporaneous sequences in eastern Australia, referred to as "Permo-Carboniferous". In this case the question of the boundary between the Carboniferous and the Permian was usually left open, but sometimes the lower tillites and the lowest fossiliferous horizons were more specifically assigned to the Upper Carboniferous. When in later years the Permian affinities of all the faunas were recognized, it was at first believed that the entire Permian was represented in Western Australia and some beds were referred to the Lower Permian, others to the Middle, still others (Wandagee and Byro series of the North-West) to the Upper Permian (Raggatt and Fletcher, 1937).

It was only when ammonoids and other fossils of great chronological value were discovered in the Western Australian Permian in greater numbers (Teichert, 1940*c*, 1942*a*, 1944*a*) that it was possible to put the correlation of the beds on a more exact basis. The conclusions thus reached were fully supported by a study of the corals. (Hill, 1943.)

Even the thickest sections known from Western Australia represent only part, almost certainly not more than half of Permian time. It is probable that sedimentation in all marine basins started more or less simultaneously very early in the Permian. The main glacial period during which most of the glacial sediments (tillites, etc.) were deposited is the Lower Permian, or Sakmarian, age. During this period up to 3,000 feet of sediments, mostly coarse clastics, were deposited over wide areas in the Irwin River district, in the North-west and in the Kimberley Divisions. The bulk of all the sediments, however, is of Artinskian age (sometimes called Middle Permian) and there are probably only comparatively small thicknesses of post-Artinskian sediments present anywhere in Western Australia. There is certainly no marine Upper Permian in the generally accepted sense anywhere in this State.

There is in general good correlation between the North-West and Desert Basin sequences. In both these areas sedimentation went on throughout Artinskian time and continued for a short time after the Artinskian. The ammonites now known from the higher marine beds of the North-West (mostly Wandagee series) include *Propinacoceras australe*, *Paragastrioceras wandageense*, *Pseudogastrioceras goochi* and *Agathiceras applanatum*.

In addition the bradyodont shark *Helicoprion*, an important zone fossil of the Artinskian, is present in the *Linoproductus* beds. In a lower stratigraphical position occur species of *Metalegoceras*, *Pseudoschistoceras* and *Thalassoceras*, partly of Artinskian and partly of Sakmarian affinities. The corals of all these beds also indicate an Artinskian to only very slightly younger age.

The exact correlation of the Western Australian Permian is of great palæogeographical significance. The Artinskian alone is in places represented by as much as 6,000 or even 7,000 feet of sediments. To enable this sequence to be accumulated in such a short time the rate of denudation of the sediment-yielding land must have been tremendous and geological processes that led to considerable uplift and the formation of a pronounced relief must have preceded and accompanied the sedimentation processes.

It is at present impossible to say to what stage of the Permian those coal measures belong that are not associated with marine beds: Eradu, Collie, Wilga, etc., except that they were probably not formed very early in the Permian when the climate of Australia was rigorous.

Triassic.

The occurrence of strata of Triassic age in Western Australia is very doubtful. In the extreme south-west of the State sandstones occur in various places in disconnected outcrops, or below the surface. In the vicinity of Donnybrook, about 30 miles E.S.E. of Bunbury (about 33° 35′ S. lat.) sandstones rest on Precambrian gneisses. At least some of these were deposited in very shallow water as evidenced by the occurrence of asymmetrical ripple-marks and of the footprints of a small four-footed vertebrate which were found in a small quarry near Brookhampton. A considerable thickness (over 1,000 feet) of sandstones and shales interbedded with a few coal seams has been penetrated by bores in the coastal plain east of Bunbury ; these may possibly be of the same age as the Donnybrook sandstones.

Another area of sedimentary rocks in the south-west corner of the State is situated in a belt of low-lying country extending from Busselton southwards to Flinders Bay and between the south-western corner of the Great Precambrian Plateau of Western Australia in the east and a ridge of Precambrian between Cape Naturaliste and Cape Leeuwin in the west. Hardly anything is known about this sedimentary area.

Some of these sediments may be equivalents of the Collie-Wilga series of Permian age and it has therefore long been customary to refer the Donnybrook sandstone to the Permian (or " Carboniferous " of earlier reports). On the other hand the existence at the time of the deposition of at least some of the sandstones of a small four-footed animal that made a narrow track and consequently must have had its body well elevated above the ground does not support a Palæozoic age of these rocks. Maitland has advocated a Triassic age for them, pointing out lithological resemblances to Triassic rocks in regions as far away as New South Wales, Tasmania and South Africa. (Maitland, 1940.)

It seems that positive evidence for such correlations is lacking. Also, it is quite possible that not all sandstones at present mapped as " Donnybrook sandstone " are actually contemporaneous. Some are no doubt younger than Palæozoic, others might well be of the age of the Collie coal measures. Some of the sandstones contain some secondary gold deposits which have been mined.

Jurassic.[11]

Distribution.

Jurassic rocks, both of the marine and of the lacustrine facies, occur rarely more than 100 miles or so inland. Proceeding from south to north the main areas of distribution of Jurassic rocks are the following: (1) Disconnected occurrences in the coastal belt north of Perth as far as Mingenew (about 32° to 29° 15′ S. lat.). Lacustrine beds only occur in this belt. (2) The vicinity of Geraldton (about 29° to 28° 40′). Marine and lacustrine beds. (3) A small outcrop on the Minilya River, about 45 miles from its mouth (114° 25′ E. long.). Marine. (4) In deep bores at Broome (18° S. lat.). Marine. (5) Disconnected outcrop areas north and south of Broome and in the vicinity of Derby. Lacustrine beds only. See Fig. 5.

Succession.

Since rocks of the lacustrine facies are at least in part older than the marine beds, they may be considered first.

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[11] The latest official geological map of Western Australia, published by the Geological Survey of Western Australia in 1933, shows a more or less continuous belt of Jurassic along or close to the west coast of the State from 30 miles north of Perth as far as the Fortescue River (31° 35′ to 21° 05′ S. lat.) and from the vicinity of Walal to King Sound (19° 55′ to 16° 20′ S. lat.). A considerable portion of this belt of rocks is now known to be of Cretaceous age.

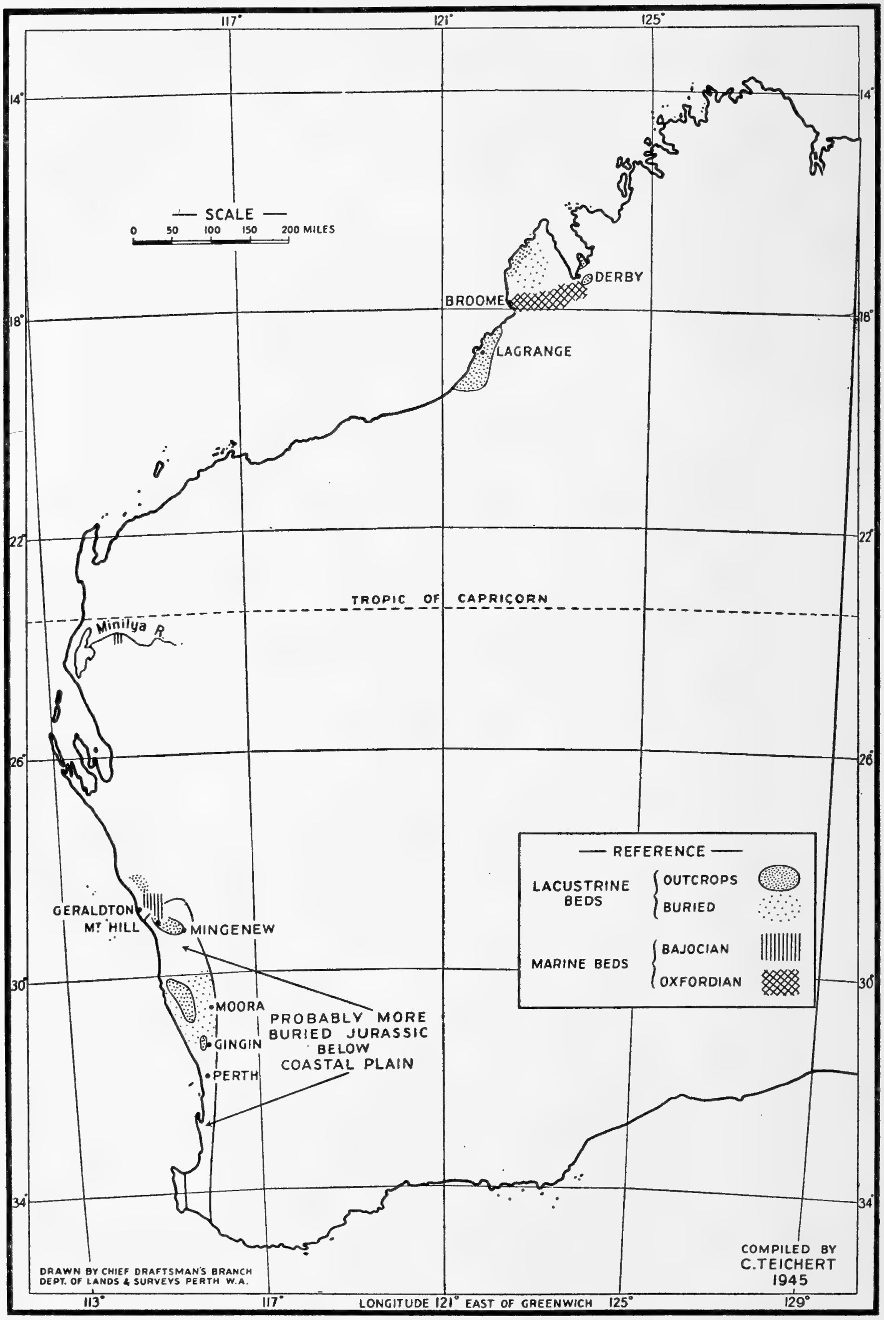

Fig. 5.—Distribution of Jurassic rocks.

Lacustrine Facies. The Coastal Plain north of Perth is a gradually widening belt of generally flat, low-lying country between the coast and the edge of the Western Australian tableland of Precambrian rocks. Most of the Coastal Plain is sandy country with scattered outcrops and small outcrop areas here and there. A common rock type is brown ferruginous sandstone and because some of these sandstones contain Jurassic plants there has been a certain tendency—perhaps not always justified—to include most ferruginous sandstones in this part of the State in the Jurassic. Perhaps the most interesting record is from the deep bore at Moora, 100 miles north of Perth, which penetrated 2,230 feet of sediments, mostly sandstones and grits. Between 1,011 and 1,147 (405 to 541 feet below sea-level) shales with *Tæniopteris* and *Otozamites* were traversed two plant genera characteristic of Jurassic lacustrine beds elsewhere in Western Australia.

At Gingin, 60 miles north of Perth, the fossiliferous Cretaceous series rests on brownish, fine-grained, clayey sandstones of unknown thickness which contain *Isoetites, Cladophlebis australis, Thinnfeldia talbragarensis, Tæniopteris spatula, Ptilophyllum pecten* and other plants of Jurassic age. (Walkom, 1944.) About 40 miles farther north at Dandarragan, Cretaceous strata rest on a series of coarse-grained red and grey sandstones which is several hundred feet thick and which may also be of Jurassic age, although no fossils have been found so far. Sandstones with *Otozamites* are also found near Mingenew in an outcrop area which may be more or less continuous with ferruginous *Otozamites* sandstones which underlie the marine Middle Jurassic beds south of Geraldton, at Mt. Hill (Campbell, 1910). Here these sandstones rise to at least 1,000 feet above sea-level, possibly higher. Towards the north, however, the lacustrine beds peter out rapidly, for only 15 miles farther north (and about 20 miles east of Geraldton) marine Middle Jurassic rests on Precambrian gneisses.

The Dongarra and Yardarino bores near the coast west of Mingenew have penetrated soft sandstones and shales to depths of 2,112 feet and 1,607 feet respectively; no fossils are available from these bores and although some authorities have suggested a Jurassic age for these beds, they may well be Cretaceous, or even Tertiary.

Summarizing we may say that lacustrine Jurassic sandstones underlie probably the whole of the Coastal Plain in the South-West Division north of Perth and that their thickness certainly exceeds 1,000 feet and may even be in excess of 2,000 feet. Considering the fact that at Mt. Hill these beds are underlying marine strata of middle Bajocian age it can be concluded that the bulk of them must be of Lower to very early Middle Jurassic age.

Similar sandstones occur in the coastal strip from somewhere south of Broome to north of Derby, in the Kimberley Division. Fine to medium-grained micaceous sandstones, sometimes cross-bedded, crop out at Pt. Gantheaume and Entrance Point near Broome as well as farther south at Cape Villaret and further inland, 50 miles south of Langrange, where tabletop hills were seen to rise 100 to 130 feet above the general level of the Desert Basin (Clapp, 1926). Such sandstones are also known to occur intermittently along the coast north of Broome as far as Beagle and Pender Bays.

At Point Tormet on the east side of King Sound, north of Derby, friable sandstones and clays with *Thinnfeldia feistmanteli, Dicroidium, Otozamites* and *Ptilophyllum* occur and a southward continuation of these beds was found near Derby, where they were traversed by a bore from the surface down to at least 300 feet below the surface. (Antevs, 1913.) From the general structure of the area it seems likely that these plant beds (Derby series) are higher than the marine Oxfordian found 20 miles farther south in a bore at Yeeda (see below) and that they are therefore of late Jurassic age, i.e. younger than the *Otozamites* sandstones of the south-west.

Marine Facies. The principal outcrop area of marine Jurassic rocks in Western Australia is in the country east and south-east of Geraldton, although the area has never been accurately mapped and the section has never been studied in detail. Its thickness may be expected to be a few hundred feet. East of Geraldton these marine rocks rest on Precambrian gneisses. A good exposure of the unconformity is seen in a railway cutting nineteen and a half miles east of Geraldton on the line to Mullewa. The Precambrian is here overlain by a few feet of conglomerate, followed by fossiliferous clays and calcareous sandstones. The rich fauna of these beds includes many pelecypods, among them species of *Cucullæa*, *Trigonia*, *Pecten*, *Ctenostreon*, *Alectryonia* and others, but also many belemnites of the *Belemnopsis* group, ostracodes, and especially ammonites. The last are of course of particular importance for the correlation of the beds. Spath (Spath, 1939) thinks that more than one ammonite zone might be represented, but in a general way he correlates the beds with the *sauzei* and *sowerbyi* zones (Lower Bajocian) of the English succession.

From the area east of Geraldton outcrops of the marine Jurassic must extend southward at least as far as Mount Hill and vicinity, though it is not known if they are continuous. As has already been mentioned, the marine strata are at Mt. Hill underlain by plant-bearing lacustrine beds.

All these marine beds may be called *Newmarracarra Series*, a name which is here proposed, but in using which it should be remembered that its scope is as yet very incompletely defined.

The Jurassic beds near Geraldton have probably been deposited on a very irregular surface. Two miles north of Geraldton, at Bluff Point, the Precambrian comes to the surface. In the Geraldton Town Bore granite was reached at 420 feet, the overlying sediments being mostly sandstone with one coal seam at 129 feet. Only a few miles east of the town, however, 1,531 feet of sandstones and shales were penetrated in the Racecourse Bore without reaching bedrock, though part of the sediments may be Permian. Some of these differences in thickness of the sediments may be due to tectonic movements and erosion after the Jurassic.

No marine Jurassic is known anywhere north of Geraldton until approximately 23° 45′ S. lat. is reached. Here a small outcrop area of quartzose and calcareous sandstones, less than 25 feet thick, was found (Teichert, 1940*a*) on the south bank of the Minilya River, which contains some pelecypods and an algal bed with *Parachætetes megalocytus* Pia. These beds occur in a small fault block between Cretaceous and Permian strata and are believed to be of the same age as the Newmarracarra series. Their distribution elsewhere in the North-West Division is at present unknown.

Finally, marine Jurassic of somewhat younger age occurs farther north, at Broome, where sandstones and shales with *Buchia subpallasi*, *Buchia subspitiensis*, and species of *Belemnopsis* have been pierced in bores between about 1,150 and 1,390 feet below sea-level. This is a typical East Indian assemblage of Oxfordian age (Teichert, 1940*b*). The total thickness of Jurassic in these bores is probably in the vicinity of 550 feet.

It is believed that these Oxfordian beds may underlie considerable portions of the coastal areas in this part of Western Australia, for an extension was found much farther inland, about 20 miles south of Derby and almost 100 miles east-north-east of Broome (Teichert, 1942*b*).

Cretaceous.

Distribution.

Cretaceous rocks in Western Australia are almost exclusively marine. They have a wide, perhaps almost continuous distribution along the west coast,

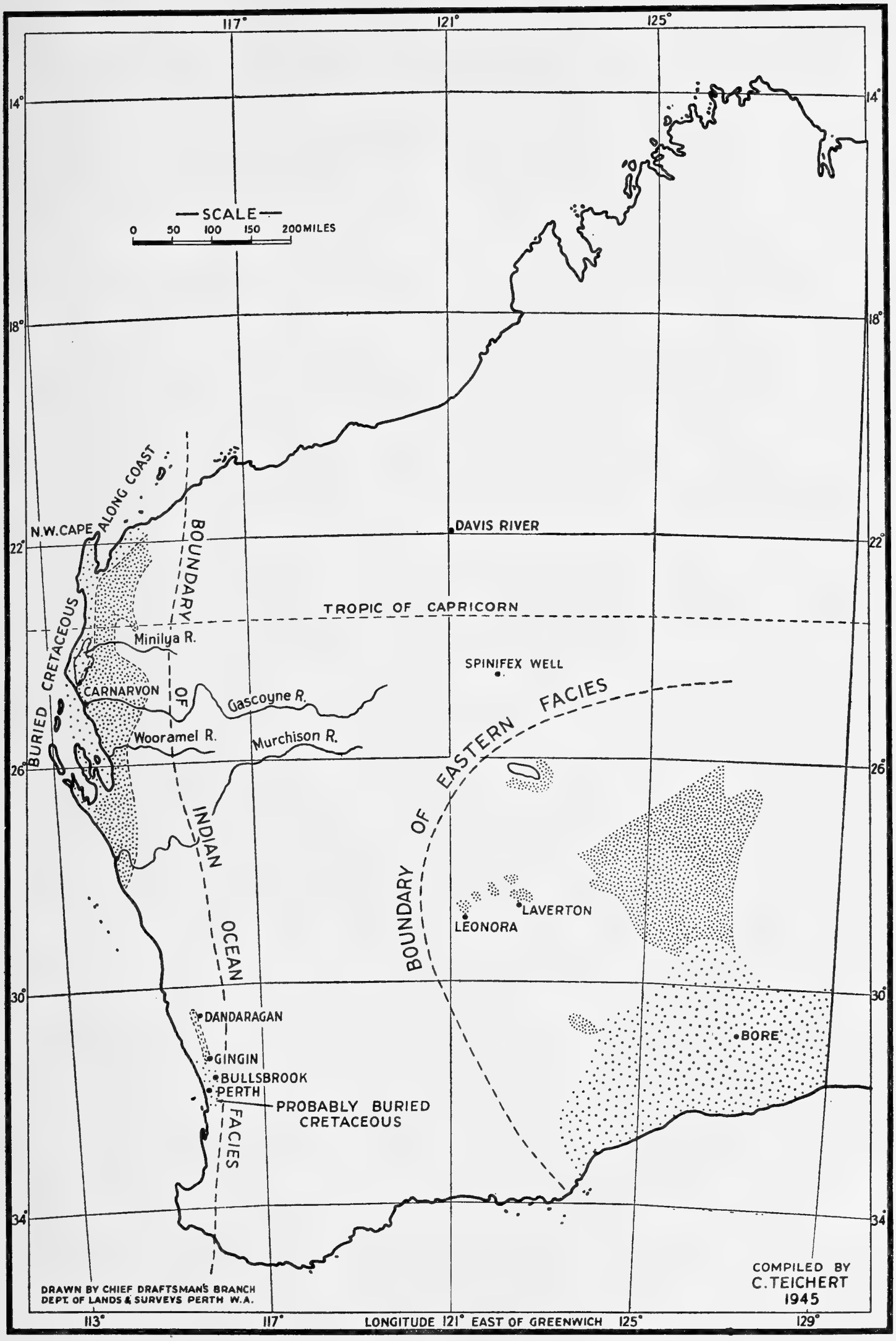

Fig. 6.—Distribution of Cretaceous rocks. Dense stippling: outcrop areas; wide stippling: buried Cretaceous.

although they are not everywhere exposed on the surface. Proceeding from the south the following areas of marine Cretaceous are known to exist:

(1) The Gingin-Dandarragan area, 60 to 110 miles north of Perth, of marine rocks.

(2) An area along the lower course of the Murchison River of estuarine and marine sediments. This is probably continuous, though not all the way in surface exposures, with the next following area.

(3) A long belt of Cretaceous rocks that begins to crop out somewhere north of Carnarvon and extends from there to the southern end of Exmouth Gulf.[12] The southern continuation of this belt has been traced in bores as far as Carnarvon, but it probably continues further south and may link up with the Cretaceous belt south of Shark Bay.

Furthermore, Cretaceous rocks occur below the Tertiary limestones of the Nullarbor Plain in the Eucla Division, though they are not exposed anywhere in this area.

In addition, there are larger and smaller outcrop areas further inland, with rocks of somewhat doubtful correlation which are now mostly regarded as Cretaceous. See Fig. 6.

Succession.

The sequences in the three main outcrop areas of marine rocks are so different that each must be described separately.

(1) *Gingin-Dandarragan Area.*

It is peculiar that, although this area is comparatively close to Perth and its geology is well known to local geologists, no detailed description has ever been published. Gingin may be regarded as the type locality of this area (Feldtman, 1933; Clarke, Prider and Teichert, 1944, pp. 274-275). The section here is as follows:

	Feet.
Upper Greensand	140
Chalk	70
Lower Greensand	20
Total	230

The Lower Greensand rests on plant beds of Jurassic age. It is very rich in glauconite and has furnished very few fossils. Its transition into the overlying chalk is somewhat gradual, the chalk itself being in places extremely fossiliferous.

However, its fossil content varies greatly even over very short distances and in places it contains very few fossils. Ammonites are rare, though a number of specimens belonging to species of the *Pachydiscus* group have been found. (Spath, 1926.) Among the more characteristic fossils are the crinoids *Marsupites* and *Uintacrinus*, a few small brachiopods, some crustaceans, and many pelecypods. Among the latter large specimens of *Inoceramus* are very common. In 1938 a specimen almost 20 inches long was excavated from a chalk deposit near Ginginup. The chalk has an interesting assemblage of detrital minerals, (Carroll, 1939) which include in addition to the light fraction (glauconite, quartz, felspar) opaque minerals, zircon, garnet, rutile, tourmaline, epidote, staurolite. amphibole, kyanite, anatase, as well as others present in minor quantities. Its

[12] The area covered by this Cretaceous belt is shown partly as Tertiary, partly as Jurassic, and partly as Permian on the latest official geological map of Western Australia (1933).

$CaCO^3$ content varies between 75% and 89% and it is thus much less pure than the British chalk, which may contain up to 98% to 99% calcium carbonate.

The boundary with the Upper Greensand is usually sharp. No fossils have been found in the latter.

North of Gingin the chalk wedges out and the greensands disappear under a cover of sand and laterite so that the exact northern boundary of the Cretaceous area cannot be stated. Under the surface it may be continuous with the larger Cretaceous area of Dandarragan which begins north of the Moore River, about 12 miles further north (31° S. lat.). This is an area of about 350 square miles, where the sequence is essentially the same as that at Gingin (Teichert and Matheson, 1944), except that the Lower Greensand contains two phosphate beds of which there is little if any trace at Gingin :

	Feet.
Upper Greensand	60
Chalk	20–40
Upper Phosphate bed	2
Lower Greensand	20–70
Lower Phosphate bed	2

This series rests on a sequence of several hundred feet of sandstones which may be of Jurassic age. The Phosphate beds consist of phosphate nodules and phosphatized wood and the Upper bed contains remains of ichthyosaurian and plesiosaurian reptiles. The chalk contains the same fossils as the Gingin chalk. The Upper Greensand appears to be unfossiliferous.

The chalk of Gingin and Dandarragan belongs to the *Marsupites* zone of the Senonian. It is of Santonian, that is Middle Senonian, age.[13] Considering the small thickness of the Lower Greensand, it is most probably still in the Santonian, whereas the Upper Greensand is almost certainly Campanian.

Nothing definite can at present be said about the southern continuation of the Gingin beds. It is possible that Cretaceous beds exist in the vicinity of Perth at more than 1,650 feet below sea-level, but these may be Lower Cretaceous (I. Crespin, in Parr, 1938, p. 71), not known in outcrops from the South-West Division.

(2) *Murchison River Area.*

There are good outcrops all along the lower course of the Murchison River (Plate VII, Fig. 1) from its mouth upstream as far as about 25 miles from the coast, where the Cretaceous sediments are faulted against the Precambrian. The sequence of rocks shown in table on p. 110 is exposed in this area (Clarke and Teichert).

The Tumblagooda sandstone is essentially a deltaic deposit that is derived from a general source area situated somewhere in the east, or more correctly probably east-south-east.

The series of sediments above the Tumblagooda sandstone was deposited in a gradually subsiding and deepening basin. The only richly fossiliferous deposit is the Toolonga chalk which contains fossils identical with those of the Gingin chalk further south and is therefore of the same age—Middle Senonian. The chalk forms cliffs on the north side of the Murchison River as far as 12 miles inland and extends northward along the coast an unknown distance, though not less than 20 or 30 miles.

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[13] The Santonian is often regarded as the lower section of the Senonian, depending on whether or not the Coniacian is included in the Senonian. I have here followed the usage adopted by S. W Muller and H. G. Schenck (*Bull. Amer. Ass. Petrol. Geol.*, Vol. 27, 1943, p. 272).

North of the Murchison River there are no outcrops almost as far as Shark Bay, 75 miles to the north, except probably along the coast which has not yet been examined geologically. There is, however, little doubt that the Cretaceous continues beneath a comparatively thin coat of drift sand and superficial travertine deposits.

The Cretaceous comes to the surface again east of Hamelin Pool (about 26° 25′ S. lat.) where unfossiliferous white and yellow shales with chert bands occur. This area is only a hundred miles from Carnarvon, where Cretaceous strata occur below the surface.

Name.	Lithology.	Fossils.	Thickness in Feet.
Second Gully shale.	Light green, hard, glauconitic shales.	—	92+
Toolonga chalk.	Mostly pure chalk, sometimes glauconitic. In many places with a 6 in. layer of phosphate nodules at the base and usually rich in chert nodules in the upper part.	Foraminifera, *Cidaris*, *Marsupites*, *Uintacrinus*, *Gryphœa*, *Inoceramus*, brachiopods.	35–120
Alinga beds.	Glauconitic shales, often sandy and with greensand pockets, grading into greensand.	Belemnites.	10–75
Thiridine shale.	Whitish to grey, siliceous shale, sometimes more massive and grading into silt-stone.	Very poor belemnite fragments, rare.	0–63
Butte sandstone.	Predominantly unbedded pure quartz sandstone, mostly loosely cemented or incoherent ("running sand"); uppermost part usually ferruginous and glauconitic.	Vertical and oblique burrows, fossil wood, rare.	75–170
Tumblagooda sandstone.	Predominantly reddish and purple sandstones, as a rule strongly cross-bedded, but grading into well-bedded sandstones above.	Vertical burrows and invertebrate trails on bedding planes.	400+

The total thickness of the Cretaceous in the Murchison River area is in the vicinity of 750 feet, probably slightly greater, though hardly in excess of 1,000 feet.

(3) *Area between Carnarvon and Exmouth Gulf.* (*Raggatt*, 1936; *Crespin*, 1938*b*.)

The best outcrops are in the northern part of this area in the Cardabia Range and the country to the east of it (Plate VII, Fig. 2). The Cretaceous beds are here thrown into a broad anticline in which Lower Cretaceous is exposed along the centre and Upper Cretaceous along both flanks.

A composite section in this area is as follows:

—	——	Thickness in Feet.
Cardabia Series. 1,070 feet.	Sandy, white to yellow Bryozoan limestone	85
	Glauconitic sand with ammonites ..	5
	Inoceramus marls	115
	Chalk, with chalky clays and calcareous claystones	865
Winning Series. 1,100 feet.	Cherts, shales and siltstones	110
	Mudstones, glauconite sands and shales ..	990

The Lower Cretaceous is not very fossiliferous, although the belemnite *Dimitobelus diptychus* is locally very abundant in greensands and shales. A small fauna of pelecypods including *Maccoyella*, *Syncyclonema*, *Trigonia* and other genera is also known. The Winning series is at present considered to be of Albian age but further evidence, especially micropalæontological, should be awaited.

In the Upper Cretaceous Cardabia series it is interesting to note that the chalk occurs fairly low down in the sequence and that Irene Crespin, on foraminiferal evidence, thinks that its age is Turonian, which is decidedly older than the chalk deposits of the south-west of Western Australia. The same author gives the age of the overlying glauconite sands from the foraminifera as Santonian, whereas Spath, who has studied the ammonoids from the same beds (Spath, 1940), regards them as Lower Mæstrichtian, although he leaves open the possibility of their being of late Campanian age. But even the latter alternative would leave a wide gap in the determination of the age of this bed by these two authorities. However, Dr. Spath's ammonites were collected by myself, whereas Miss Crespin's foraminifera came from Dr. Raggatt's collection and there is thus of course the possibility that our collections might not have been derived from strictly the same horizon. Spath suspected that even my ammonite collections might represent two closely related biozones and not one as I had thought in the field.

The ammonites in this bed are an interesting assemblage which closely resembles the fauna of the Valudayur and Aryalur groups of south-eastern India and includes species of *Paraphylloceras*, *Phyllopachyceras*, *Pseudophyllites*, *Hauericeras*, *Kossmaticeras*, *Diplomoceras*, *Glyptoxoceras* and *Eubaculites*.

The top Bryozoan limestone may be either Upper Mæstrichtian or Danian in age. The *Inoceramus* marls below the ammonite greensand may correspond to the Gingin and Toolonga chalk of the South-west Division, although the faunas are somewhat different.

The total thickness of the Cretaceous, combined from various sources is given by Raggatt as over 2,000 feet. From bore logs and surface data given by Forman (Forman, 1938) it appears that there is a general increase in thickness in a westerly direction from about 1,600 feet east of Cardabia Range to something like 2,200 feet west of Cardabia Range, where the Cretaceous is buried under Tertiary rocks. Raggatt suggests a thickening of the Cardabia series of about 200 feet in a southerly direction between Cardabia Range and Carnarvon.

Cretaceous outcrops extend from Cardabia Range southwards as far as the Lyndon River. South of the Lyndon outcrops of the Cretaceous are scattered and far between, though I have found Upper Cretaceous fossils in a limestone ridge about 15 miles south of the Minilya River and east of the big Salt Lake. This occurrence is due west of the outcrops of the siltstones of the Winning series at Barrabiddy Hills (Trigonometrical Station K 56) and it is possible that a more or less continuous west-dipping sequence of Cretaceous exists in this area.

(4) *Buried Cretaceous of Eucla Division.*

The Tertiary limestone which covers large areas in this Division has been penetrated by a few deep bores which have reached the underlying strata.[14]

[14] Boring for Water on the Transcontinental Railway Line, *Geol. Surv. West. Aust., Ann. Progr. Rep. f.* 1914, pp. 13–14, 1915.

Cretaceous fossils have only been found in one of the bores, near the intersection of the railway line and the 127th parallel E. long., where the section is as follows :

	Feet.
Eucla limestone (Miocene)	603
Shales	667
Fine and coarse sand with hard bands and granite boulders	74
Granite	28

Below the Eucla limestone, presumably in the shales, specimens of *Aucella hughendenensis* and *Maccoyella corbiensis* were obtained. These are two characteristic fossils of the eastern Australian Lower Cretaceous and indicate an extension of the beds of that age into Western Australia. Other bores in the Nullarbor Plain reached the shales below the Eucla limestone at depths varying from 400 to 900 feet below the surface. The Precambrian basement (" granite ") was reached in two bores along the railway line and the thickness of the presumably Lower Cretaceous shales and sandstones was found to be 741 feet and 815 feet respectively. Farther south towards the coast the Cretaceous obviously becomes thicker, for at Madura, on the edge of the Hampton Escarpment, 1,135 feet of sandstones, greensands and shales of presumably Cretaceous age were penetrated below 905 feet of Eucla limestone but no bedrock was reached.

It has sometimes been stated that these beds may come to the surface somewhere north of the Nullarbor Plain, where they might be continuous with the Wilkinson Range series of sandstones and boulder beds to be discussed next. However, the geology of this belt is unknown and any such correlations are at present entirely conjectural.

(5) *Possible Cretaceous of the Interior.*

Special mention must be made of a sedimentary area of possibly quite considerable extent in the interior of Western Australia about which, unfortunately, very little is as yet known (Talbot and Clarke, 1918). Between Virginia Range and Warburton Range, for a distance of over 200 miles, the country is entirely composed of horizontally bedded, slightly compacted, unmetamorphosed sandstones and claystones, with occasional boulder beds or residuals of such. Current-bedding is common in the sandstones and scratched and facetted pebbles have been collected from the boulder beds so that a glacial origin of these beds suggested itself. This series has been termed *Wilkinson Range* series. Its beds probably extend westward to the neighbourhood of Laverton and Leonora and south-westward as far as the Ponton River, although outcrops are not continuous and in some places only residuals of the boulder beds are left. Another possible extension is found farther north to the south, east and north-east of Lake Carnegie, where boulder clays with scratched and faceted pebbles have been found in numerous localities. Mostly they form flat-topped hills of whitish clay and clayey rocks which rest unconformably on the Precambrian Nullagine series.

Southward there seems to be an extension of the same series in the direction of the Nullarbor Plain. The official Geological Map of Western Australia of 1933 shows an area of about 30,000 square miles occupied by the Wilkinson Range series, but if all the sediments mentioned here are of the same age, the original area covered by them must have been at least 60,000 square miles.

However, it must be remembered that our knowledge of these sediments is as yet of the scantiest nature and that nothing is known about the northern and eastern continuation of the sedimentary area.

In the absence of fossils a Cretaceous age has been advocated for the Wilkinson Range series because of its lithological similarities with presumably

Cretaceous sediments in South Australia. It must, however, be remembered that glacial sediments of Permian age are widely distributed in Western Australia and that a Permian age of the Wilkinson Range series cannot at present be ruled out.

Other doubtful reports of sediments of possibly Cretaceous age come from widely separated points in the interior of the North-West Division (Chapman, 1933). Cherts with coccoliths occur on the Davis River near Survey Mark CC.88 (approx. 22° S. lat., 119° E. long.) and glauconitic sandstone containing doubtful casts of foraminifera and radiolaria at Spinifex Well (24° 38′ S. lat., 119° 38′ E. long.). There is no definite proof of the Cretaceous age of either of these deposits, which may well be remnants of the sediments of the Miocene transgression.

(6) *Lacustrine Beds.*

Considering the wide distribution of Cretaceous in lacustrine facies in central and eastern Australia, the meagre record in Western Australia of such deposits of proved Cretaceous age is surprising. The only lacustrine, plant-bearing sandstones and shales at present regarded as of Cretaceous age are in the vicinity of Bullsbrook, 30 miles north of Perth, where they appear to be faulted down along the Darling fault scarp. They contain *Thinnfeldia*, *Tæniopteris*, *Nilssonia* and *Elatocladus*. (Walkom, 1944.)

Tertiary.

Distribution.

Tertiary strata are widely distributed in Western Australia, which proves a link between eastern Australian and East Indian faunal facies. Since Tertiary rocks have their main distribution in the coastal districts it may be convenient to consider the different areas in a clockwise direction :

(1) Nullarbor Plain (Eucla Division). Tertiary limestones cover an area, large and semi-circular, with a radius of about 175 miles, with its centre near Eyre on the Great Australian Bight, and extending from Israelite Bay in the west as far as and beyond the South Australian boundary in the east.

(2) About 100 miles to the west in the vicinity of the mining town of Norseman is an area of disconnected outcrops of limestones, dolomites and sponge spicule beds.

(3) Further west is a belt of sandy and clayey rocks extending from the vicinity of Ravensthorpe to west of Albany, in places up to 30 miles wide.

(4) On the west coast Tertiary rocks have been pierced in bores below Perth. It is quite possible that they are more widely distributed below the South-west Coastal Plain.

(5) A belt of Tertiary rocks extends from somewhere north of Carnarvon in the North-west Division as far as North-west Cape. It is about 200 miles long and on the average about 20 miles wide. However, Tertiary outliers may exist in this vicinity as far as 100 miles inland.

(6) Lacustrine beds in the East Kimberley and North-west Divisions of doubtfully Tertiary age.

Succession.

Considering the great differences in stratigraphy between most of the abovementioned areas, it seems best to discuss the succession in each area first, before a summary of Tertiary stratigraphy of the State can be given. For complete references to the literature the reader is referred to Singleton (1941).

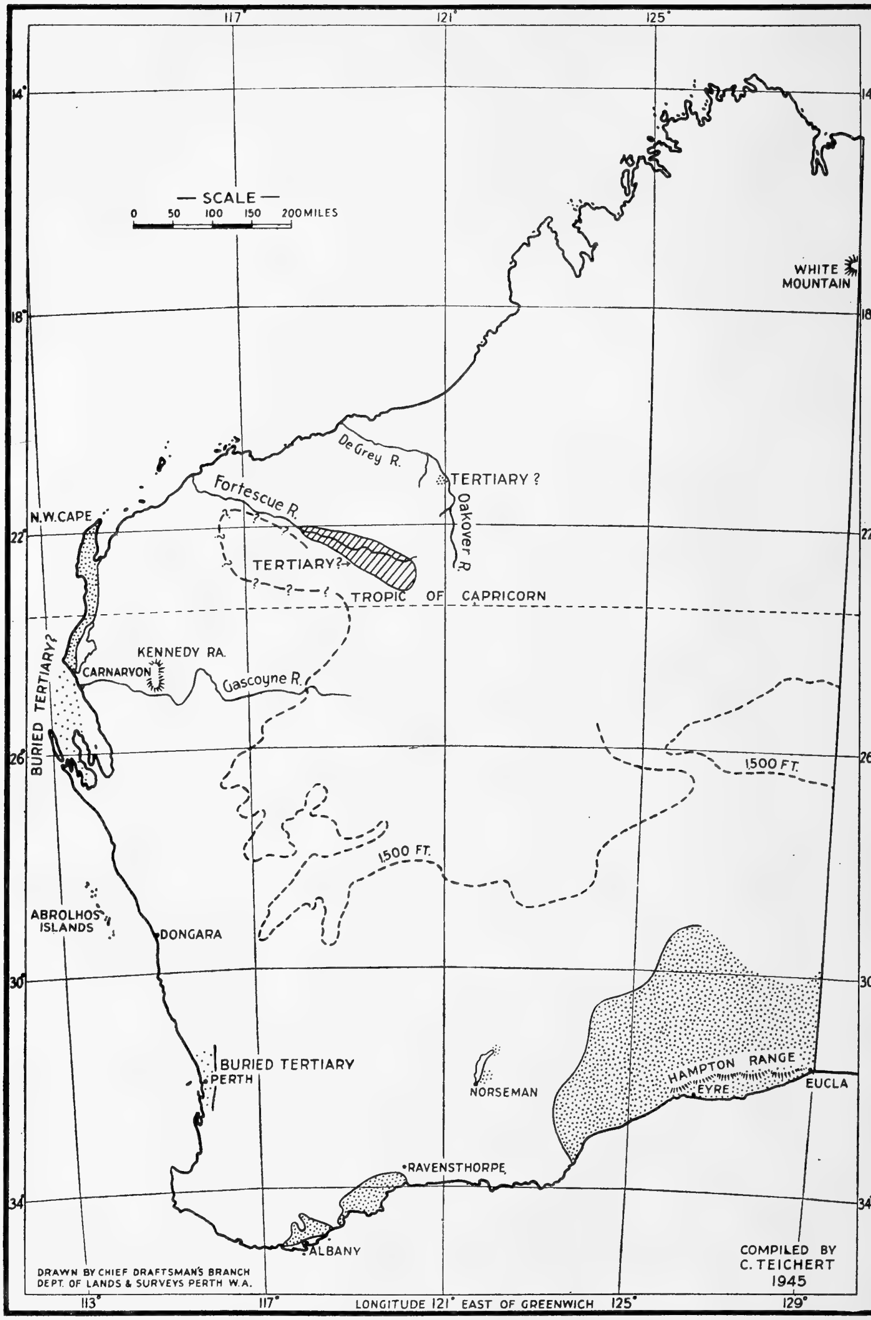

Fig. 7.—Distribution of Tertiary rocks. Dense stippling: outcrop areas; wide stippling: buried Tertiary; oblique ruling: Fortescue River basin. The 1,500-feet contour (adapted from Contour Map of Western Australia, South Sheet, 1913) may indicate the approximate northern limit of the Miocene submergence of the Western Australian Shield. North of the Tropic of Capricorn insufficient data are available for a continuation of the line.

(1) *Nullarbor Plain.*

The Nullarbor Plain is one of the most remarkable geological and physiographical features of Western Australia. It is a limestone plateau which rises imperceptibly from the coastal escarpment inland and which appears perfectly level when traversed on the ground. From the air very slight large-scale buckling and faintly indicated drainage patterns, too faint to be recognizable from the ground, may be seen here and there. The area of the Western Australian portion of the Nullarbor Plain may be estimated as between 20,000 and 25,000 square miles. The nature of the country may be visualized from the fact that one section of the Trans-Australian Railway crosses the Nullarbor Plain in a perfectly straight line for 330 miles—the longest straight stretch of railway in the world.

The surface of the plateau is formed by limestone which breaks off towards the south in a steep escarpment about 200 to 250 feet high, known as " Hampton Range ". This escarpment forms the coast south-west of Eyre, but from Eyre it bends away from the coast and extends in a slight northerly curve as far as Eucla on the South Australian border. Here it reaches the coast again and continues into South Australia.

The plain is almost completely treeless. Much of it is covered with low salt bush, but some parts are quite desert-like. Although the area receives several inches of fairly reliable rainfall per year there is no surface drainage, most of the water disappearing below the surface through cracks in the limestone.

This limestone is known as *Eucla Limestone.* It is in general very fossiliferous and contains in places large numbers of bryozoa, pelecypods and gastropods. Unfortunately, the state of preservation of the fossils is generally discouraging and the fauna has never been studied in detail. Most of the fossils are preserved as internal moulds only and identification is thus made difficult.

From the nature of the terrain it may be concluded that only a small thickness of beds is accessible in outcrops over the entire area of the Nullarbor Plain and in the absence of erosion channels and other natural excavations (other than caves which are as yet very incompletely explored) our knowledge of the vertical section of the Eucla limestone is derived from the few bores which have penetrated it. From these it would seem that the limestone is of very uniform composition throughout and that along a north-south section at 127° E. long. its thickness increases from about 485 feet near the railway line to over 900 feet at the Hampton Range escarpment.

Although no palæontological work has been done on the Western Australian side the eastward extension of the Eucla limestone is a little better known and its Miocene age has been established in South Australia. Singleton believes that the Eucla limestone may range downward into the Oligocene.

Of considerable interest is the occurrence of reef-building corals near Forrest, only 50 miles inside Western Australia on the railway line west of the South Australian border. This apparently indicates an influx of north-western faunas into this area, but unfortunately the occurrence has not yet been investigated in the field. Specimens were collected and sent to me by members of the Royal Australian Air Force stationed there during the war.

(2) *Norseman Area.*

Tertiary rocks occur in depressions near Norseman and in the general vicinity of Lake Cowan (Plate V, Fig. 5). These are no doubt remnants of a sheet of sediments which was once continuous with the Tertiary sediments in the east and in the south-west. Norseman is a mining centre, situated 350 miles east of Perth and over 100 miles north of Esperance on the south coast. It lies well inside the Great Western Australian Plateau of Precambrian rocks, near the southern end of Lake Cowan, one of the major " salt lakes " of the State.

Like other Western Australian " lakes ", Lake Cowan has a perfectly level floor, most of which is covered with a deposit of salt mud. The " lake " is usually dry, although a few inches of rapidly evaporating water may accumulate after heavy rains in the winter.

Three main rock types are known which occur in scattered outcrops on the floor and along the shores of Lake Cowan : fossiliferous limestone, unfossiliferous dolomites, and sponge spicule beds (see Clarke, Teichert and McWhae).

The limestones (in places dolomitized) contain a fairly rich fauna, mainly Bryozoa, pelecypods and gastropods of Middle Miocene age and of eastern Australian affinities. The sponge spicule beds are usually soft sandstones with a varying amount of sponge spicules which include a great variety of monactinellid, tetractinellid and lithistid types. In places these spicules make up the bulk of the rock which may then be known as spiculite or spongolite. The best known occurrence of this rock type is near the (now abandoned) town site of Princess Royal, 4½ miles north of Norseman, where these beds are well exposed in a depression in the Precambrian. Their thickness is little over 20 feet. Nowhere do the Tertiary strata in this area seem to exceed 50 feet in thickness.

(3) *South Coast West of Ravensthorpe.*

This belt of Tertiary sediments known as Plantagenet Series begins on the coast approximately south of Ravensthorpe and extends westward as far as Albany, the principal harbour on the south coast. The rocks are silts and fine-grained sandstones, in places rich in sponge spicules and not unlike some of the Lake Cowan spongolites mentioned above. They rest in patches on Precambrian granite which forms the coastal cliffs in many places. Their maximum thickness is not exactly known, but may be in the vicinity of 200 feet. In addition to sponges the strata contain a rich fauna of pelecypods and gastropods as well as Bryozoa, echinoids, brachiopods, cephalopods and plant impressions. Chapman and Crespin (1934) determined the age of these beds as Lower Miocene, but Miss Crespin has informed me that she now regards them as Middle Miocene, that is of the same age as the Norseman limestones.

It may be assumed that the Plantagenet series was once continuous with the Tertiary deposits near Norseman and that the intervening cover of sediments has been removed by Upper Miocene and post-Miocene erosion.

(4) *South-West Coastal Plain.*

Many deep bores have shown the South-West Coastal Plain to be underlain by a considerable thickness of sediments. In places these have been proved to be of Jurassic and Cretaceous, as already described, but in places they are younger. The only place where the existence of buried sediments of Tertiary age has been proved by palæontological evidence is the section below Perth. (Parr, 1938.) The thickness of sediments below the Coastal Plain is here known to be in excess of 2,000 feet. The rocks are mostly sandstone and shale and Eocene foraminifera have been recorded in cores from depths between 120 to 780 feet. More recently a rich fossiliferous black shale has been found at a depth of 60 to 100 feet below sea-level at Government Garden, Perth, but its fauna has not yet been studied. From the study of a few foraminifera Miss Crespin suggests an Eocene age, but considering its high position in the sequence, it might well be somewhat younger.

It is quite possible that Tertiary strata have a wider extent below the Coastal Plain north of Perth, but nothing definite is known at present. However, it might be well to be reminded at this stage that the Coastal Limestone of Pleistocene age has often been classified as Tertiary and that, therefore, " Tertiary " is mentioned from the South-West Coastal Plain in a number of geological reports.

(5) *North-West Division.*

The most complete Tertiary sequence in Western Australia is known from the coastal country north of Carnarvon between approximately 24° 20′ and 21° 40′ S. lat. These beds form low coast ranges or coastal platforms and near the northern end of the belt they are thrown into low anticlinal structures of which Rough Range and Cape Range, extending as far as North-West Cape, are examples (Plate V, Fig. 6).

The oldest rocks in this belt are of Upper Eocene age. They are known from Cape Cuvier and Red Bluff, 40 to 50 miles north of Carnarvon, as well as from the vicinity of Giralia, south of Exmouth Gulf. The rocks are foraminiferal and bryozoan limestones, often with rolled quartz grains ; at least in the Giralia anticline they do not seem to be more than 30 feet thick. Characteristic foraminiferal genera in these beds are *Discocyclina*, *Pellatispira*, *Asterocyclina* and *Nummulites*. Singleton has given the name *Giralian* to this series.

Next younger in the sequence seem to be limestones with *Lepidocyclina dilatata*, *L. papuanensis* and *L. chapmani*, whose age has been somewhat disputed. At first they were determined by Chapman (1927) as Oligocene, but a few years later the same author (Chapman, in Condit, 1935, p. 865) seems to have changed his opinion and to have referred the same beds to the Lower Miocene. In the same way Irene Crespin (1938*a*) seems to be inclined to stress the Lower Miocene affinities, but Singleton (1941) pointed out that *C. papuanensis* was known from Tertiary *d* in East Borneo and consequently he referred the rocks in question back to the Upper Oligocene.

Of unquestionable Miocene age are limestones with *Lepidocyclina murrayana* and *L. insulænatalis*, associated with nephrilepidines and with *Cycloclypeus*. Still higher in the Miocene are limestones with *Marginopora vertebralis*, *Flosculinella bontangensis*, *Trillina howchini* and nephrilepidines, which in turn are overlain by white coralline limestones which may range upward into the Pliocene.

The entire Tertiary sequence is possibly not more than 70 feet thick. Its fauna shows close affinities to the East Indian Tertiary and the following correlations between the East Indies and Western Australia have been suggested :

East Indies.		Western Australia.
Pliocene	*h* *g*	? Coralline limestone.
Miocene	*f*	Limestones with *Trillina howchini*, *Flosculinella bontangensis*, etc.
	e	Limestones with *Lepidocyclina murrayana*, *L. verbeeki*, etc.
Oligocene	*d* *c*	Limestones with *Lepidocyclina dilatata*, *L. papuanensis*, etc.
Eocene	*b* *a*	Limestones with *Discocyclina* and *Pellatispira* (" Giralian ").

Tertiary rocks, though at present best known from a narrow coastal belt, must be present much farther east, at least as far as 100 miles or so inland (Teichert, 1944*b*), for specimens of Miocene *Aturia clarkei* and a small associated fauna have been found on the east side of the Kennedy Range, north of the Gascoyne River.

(6) *Lacustrine Beds of Doubtful Age.*

No marine Tertiary beds are at present known from anywhere north of North-West Cape, and non-marine occurrences are not undisputed. E. T. Hardman, in 1884, discovered a small occurrence of fossiliferous chert in the East Kimberley Division near the Trigonometrical Station J 40 in a small range known as White Mountains,[15] and this bed was usually regarded as of Upper Tertiary age until Chapman described its fauna more fully in 1937 (Chapman, 1937). This includes *Planorbis hardmani*, *Planorbis* cf. *essingtonensis*, *Bullinus* sp. as well as remains of foraminifera, sponges, ostracodes, and insect and plant fragments. Chapman concluded that these beds, in common with similar deposits in Central Australia and Queensland are Pleistocene.

More recently (Teichert and Matheson, 1947), it has been shown that these lacustrine beds are much thicker than was previously known and that they cover an appreciable area in the White Mountain Range south-east of Trigonometrical Station J 40 (Plate VII, Fig. 4). The sequence is here as follows :

	Feet.
Planorbis chert	5
Siltstone	10
Chert	30
Siltstone	55
Marl	215
Siltstone with basal chert	55
Total thickness	370

The whole series is slightly folded and east of the Trig. Station, where the most complete series was observed, it dips at 25° to the N.E. These observations seem to support Singleton's suggestion that the " physiographical setting " of the beds may indicate a Pliocene rather than a Pleistocene age.

A large area of sandstones, limestones and cherts of moderate thickness is known from the valley of the Oakover River (about 21° S. lat.) in the North-West Division, where they rest with a violent unconformity on the Nullagine System. The beds have been strongly eroded and form steep escarpments and isolated mesas. No fossil evidence is available to support the correlation of the Oakover beds with the Tertiary and considering the fact that the occurrence is not so far from the south-eastern edge of the Desert Basin of Palæozoic rocks the beds might well be older.

A very much larger area of relatively young sediments occupies a sunkland through which the Fortescue River flows in its upper course between the Hamersley-Ophthalmia Plateau in the south and the Northern Plateau in the north. Over 3,000 square miles of this sunkland are covered with sediments which range from fine silt to pebble beds. Their thickness is unknown, but exceeds 100 feet (Talbot, 1920). They are believed to be lake deposits and may reasonably be expected to be younger than Miocene, though it is impossible to state at present whether they are of Pliocene or Pleistocene age.

Of somewhat similar age are possibly the Brumby Creek beds in the valley of the Ashburton River further south (about 119° E. long., 24° 15′ S. lat.). The limestones with chert bands are probably of lacustrine origin.

Summary of Tertiary Palæogeography.

During the Palæogene almost all of Western Australia must have been above sea-level, since Upper Eocene and, probably, Upper Oligocene limestones

[15] Hardman, Wade and others refer to this range as " Mt. Elder Range ". Mt. Elder, however, is a hill quite separate from the line of the White Mountains.

are restricted to a narrow belt near the coast of the North-West Division, and since there is no indication of a former wider distribution of such rocks.

It was first during the Miocene that a considerable portion of Western Australia was submerged. The amount of the submergence may have been approximately 1,500 feet below the level at present occupied by this part of the continent, and the present 1,500 feet contour may therefore give a rough idea of the position of the coast line at that time. Deposits of this sea are the Eucla Limestone, the Plantagenet Beds, the Norseman limestones and spongolites, foraminiferal limestones of the North-West Division, and the *Aturia* beds of the Kennedy Range. It is quite possible that additional sedimentary outcrops will be found in salt lakes and other depressions of the North-west and Eastern Divisions.

At the end of the Miocene, perhaps already in Upper Miocene time, the land emerged again and the sea withdrew and probably continued to cover but insignificant parts of the continent. The following Pliocene was of great importance for the evolution of the present topographical features of large parts of Western Australia because it was most likely during this time that an almost continuous laterite layer was formed, probably as a hard pan under humid conditions (Clarke, Prider and Teichert, 1944, pp. 47-50). This layer, which is also called " duricrust " in Western Australia has been much eroded since Pliocene times, but it still covers quite considerable parts of the North-West, South-West and Eastern Divisions, and even where the cover is not continuous now, there are numbers of eroded remnants to be found. The effect of the presence of this rather resistant cover is that much of the bedrock in these areas is concealed and the study of the geological structures is rendered difficult.

It is possible that the sedimentary filling of some of the salt lakes dates back to Tertiary times (see under " Pleistocene ").

Tertiary Vulcanism.

Western Australia seems to have been entirely free from any signs of volcanic activity from early Palæozoic until Tertiary time. The volcanic rocks that are supposed to belong to the latter period may therefore receive a brief mention.

In the far south-west of the State there is a small basalt occurrence at Bunbury which is older than the Pleistocene Coastal Limestone. From its occurrence on the coast where it is now being strongly eroded by the ocean waves, it may be concluded that its eruption perhaps did not precede the formation of the Coastal Limestone by a very long time and that the basalt is not older than Late Tertiary. A few basalt occurrences of presumably the same age are found along a line south of Bunbury as far as the south coast (Edwards, 1938).

Another area of comparatively young vulcanism is found in the West Kimberley Division, where the Permian rocks are pierced by numerous plugs of leucite rocks of highly unusual composition (Wade and Prider, 1940).

Most of these form conspicuous physiographical features standing out as cones or sharp-crested hills above the sedimentary plains surrounding them. From their youthful appearance it seems unlikely that they should be of any considerable age and they are probably not older than late Tertiary.

PLEISTOCENE.[16]

Deposits of Pleistocene age must have a wide distribution in Western Australia, but on the whole little attention has been paid to them ; often their age might not have been recognized ; and sometimes they may be hard to

[16] Western Australian deposits of Pleistocene age, particularly those of marine and of æolian origin, have sometimes been classified as Tertiary, sometimes they have been included with Recent or " sub-Recent " deposits.

distinguish from Recent deposits. The following survey of Pleistocene sediments of Western Australia is, therefore, very incomplete, but as rocks of this age may reach appreciable thicknesses they must not be neglected. These rocks are best considered in three major groups according to their origin : (1) marine, (2) æolian, and (3) lacustrine and fluviatile.

(1) *Marine Deposits.*

The coast of Western Australia from the extreme south-west northward at least as far as Port Hedland, but probably farther north, is lined with a narrow and discontinuous belt of limestones and well-bedded calcareous sandstones which in some places are richly fossiliferous. The fossil assemblages in these rocks bear a strong resemblance to the recent faunas along the same coast although sometimes they seem to contain a certain proportion of species that are not now known to occur at the same latitude. Well-known shell deposits are those along the Swan River in the vicinity of Perth (Peppermint Grove, Minim Cove and others) which rise to 23 feet above sea-level and contain some species of molluscs which at present do not occur south of Geraldton, 250 miles to the north.

In Perth limestones have been pierced by bores down to a depth of 180 feet below sea-level (Forman, 1933), and it seems reasonable to conclude that these deeper limestones are at least partially marine, even though it is known that in places the overlying æolian limestones reach below sea-level.

Contemporaneous deposits are probably the shell beds at the bottom of the Swan River estuary which occur at a distance of up to eight miles from the present coast and which contain a rich fauna of Recent species such as *Ostrea angasi*, *Chama limbula*, *Gafrarium sulcatum*, *Dosinia sculptilis*, *Chlamys asperrimus* *Polinices conicus* and many others (Reath, 1925).

Elsewhere small coral reefs occur in the same beds. Two which I have been able to study are the Leander Point Reef at Denison, 40 miles south of Geraldton, and a reef in Salmon Bay on the south coast of Rottnest Island, off the mainland coast at Fremantle. Both reefs are flat-topped and rise to about 10 feet above mean sea-level. The association of reef corals in both is very much like that now found in the Abrolhos Islands, although one is 30 miles, the other 200 miles south of the southernmost coral island of that group. I have seen small colonies of reef corals too small to be called coral reefs, much farther south along the coast as far as Canal Rocks, 10 miles south of Cape Naturaliste (about 33° 50′ S. lat.). In the North-West Division I have observed similar fossiliferous limestones in the vicinity of Cardabia Station near Maud Landing and near Yardie Creek, 50 miles south of North-west Cape. Here these limestones contain the tropical mollusc fauna characteristic of these latitudes at the present day.

The aerodrome of Onslow (about 23° 40′ S. lat.) in close proximity to the coast and only one to two feet above high water level (about nine feet above mean sea-level) is built on the surface of an emerged coral reef, but this is of course well inside the tropical reef belt of the present day. A bore near the township of Onslow penetrated solid limestone from 30 to 214 feet below sea-level, before entering a thick shale section of over 1,500 feet. Thus it is most likely that the marine Pleistocene limestone in this general area is from 180 to 220 feet thick. Little is known about the distribution of this limestone farther north, but it may occur as far north as the west coast of Dampier Land, north of Broome.

In most places this marine limestone belt is quite narrow, but where the coastal country is very flat or where embayments existed, they might be found up to a few miles inland from the coast. Thus at Cardabia and at Perth the limestone occurs several miles from the present outer coast.

The core of older coral reefs in the four main groups of the Abrolhos Islands, 40 miles off the coast opposite Geraldton in the Indian Ocean, also belongs to this

same limestone formation. The top of these old reefs is now generally 6 to 12 feet above mean sea-level (Plate VII, Fig. 3) (Teichert, 1947). It should perhaps be mentioned that the coral islands of the Sahul Shelf, off the north-western coast of the Kimberley Division, are of an entirely different type. I have examined aerial photographs of Seringapatam Reef, Cartier Reef, Browse Island and Adele Island and found that none of them has any emerged reef limestones. They are similar to some reefs of the inner belt of the Great Barrier Reef of Queensland.

It seems very probable that much, if not most, of the continental shelf along the west coast is covered by limestone deposits of the same age. It has already been mentioned that the thickness of the limestone is in the vicinity of 200 feet in such widely separated places as Perth and Onslow, which is not likely to be a mere coincidence. On Rottnest Island, 12 miles off the coast west of Fremantle, 210 feet of limestone were found in a bore below 20 feet of superficial sand, but elsewhere on the island the same limestone crops out above sea-level. There is thus evidence that the continental shelf, at least down to the 35-fathom line, is covered with a considerable deposit of Pleistocene limestones. Not all of these submerged limestones, however, may be marine; some may belong to the æolian group to be discussed next.

All these rocks are older than the æolian limestones which, as will be shown below, are not younger than late Pleistocene. It is reasonable to assume that the marine limestones were formed during an interglacial period of the Pleistocene, when the climate was slightly warmer and the sea-level stood somewhat higher than at the present day. They may be deposits of either the Mindel-Riss or of the Riss-Würm interglacial stage.

The Mindel-Riss Interglacial was probably the longer of the two and at times its climate was warmer than of the present day. The marine coastal limestones may therefore well have been formed during this stage.

The fact that they are now exposed above sea-level is chiefly due to the negative eustatic 5-m. shift of sea-level in mid-Recent time for which there is abundant evidence elsewhere in Australia and in the South-West Pacific area (Browne, 1945).

(2) *Æolian Deposits.*

In close association with the marine limestones occur dune limestones which form a very conspicuous physiographical feature along something like 1,500 miles of coast in Western Australia. These æolian limestones are generally referred to as " Coastal Limestone ", a term in which the underlying marine section may or may not be included. They form a belt up to six miles wide, though usually narrower, extending from Bremer Bay on the south coast (about 119½° E. long.) westward around the south-western corner of the continent and northward along the west coast as far as North-West Cape. Farther north they seem to be very scattered, though I have observed dune limestone hills from the air several miles north-east of Port Hedland (about 20° 20′ S. lat.) and there seems to be some evidence for them as far north as Cape Villaret, 25 miles south of Broome and the west coast of Dampier Land, north of Broome. But even in the south, along the west coast between Cape Leeuwin and North-west Cape, the dune limestone belt is by no means unbroken, although it has never been completely mapped and large parts of it have probably never been seen by geologists. Some areas of outstanding development of dune limestone topography are:

(1) The Precambrian ridge between Cape Leeuwin and Cape Naturaliste, where large caves exist in the Coastal Limestone. In deposits laid down in these caves numerous remains of extinct marsupials have been found which include *Diprotodon*, *Nototherium*, the Tasmanian Devil, the Marsupial Lion, the

Koala Bear, extinct giant kangaroos and others, though these must belong to a somewhat later time, perhaps very late Pleistocene or very early Recent.

(2) The vicinity of Perth (King's Park, Mosman Park, etc.) and the outlying islands of Rottnest, Garden Island and others. In many places the dune limestones can be seen outcropping at sea-level, as for example on the east coast of Rottnest Island, where they are now subjected to wave erosion.

(3) Separated from this locality by almost 300 miles of mostly exceedingly monotonous coast line are thick dune limestone deposits north of the Bowes River, about 30 miles north of Geraldton. Between Perth and the Bowes River there are a great many occurrences of smaller limestone cliffs, probably at least partly of æolian origin. The coast is fringed by many limestone shoals, reefs and islets which make it quite dangerous to navigation. I have frequently flown along this coast but in only a very few places has it ever been visited by geologists.

(4) Dune limestones up to 30 feet thick are found on the larger islands (East and West Wallaby and North Island) of the Abrolhos Island group. They overlie the Pleistocene reef limestones mentioned above and are now everywhere dissected by marine erosion.

(5) High dune limestone ridges seem to exist along the coast north of about 27° S. lat. on Tamala[17] and on the peninsula separating Freycinet Bay from the Indian Ocean; from here the limestone belt probably continues across South Passage to Dirk Hartog Island, where it rises to 608 feet above sea-level. No part of this coast has ever been examined by geologists.

In many places and along certain horizons the dune limestones are penetrated by a meshwork of root-like structures which are the calcareous fillings of cavities left by roots of plants. Periods of fixation of the old dunes are thus evident. Everywhere, of course, the limestones are very strongly false-bedded.

In some localities these limestones occur in places where it would have been impossible for them to be formed under physiographic conditions resembling those of the present day. This is especially true for the dune limestones of the Abrolhos Islands, and it is most likely that all these æolian limestones were formed during a glacial stage of the Pleistocene, when the sea-level stood lower than now and large parts of the Western Australian shelf were exposed to wind erosion. The Western Australian shelf varies in width from a few to fifty to sixty miles and its average depth below sea-level is now 20 to 25 fathoms. It must therefore have been dry land repeatedly and for prolonged period during the Pleistocene. The evidence as to the origin of the Western Australian dune limestones thus agrees well with that proposed for similar deposits in Victoria, Bermuda and elsewhere (Hills, 1939).

As mentioned above, caves in these limestones contain deposits with extinct marsupials which are generally regarded as Pleistocene, though they may possibly be of early Recent age. The dune limestones themselves can, therefore, not be younger than late Pleistocene.

The fact that in many places the transition from the underlying marine limestones to the dune limestones is gradual suggests that the latter must have been formed during the glacial stage immediately following that inter-glacial stage in which the marine limestones were laid down, probably the Riss, or possibly the Würm stage. The material for the dune limestones must have been largely derived from the underlying marine limestones which as has been shown

[17] In this vicinity the British Admiralty Chart (1056) notes " high sandstone cliffs " of 850 and 1,000 feet. Seen from the air at a distance of twenty to thirty miles, these ridges rise conspicuously above the general level of the plateau, so that I have little doubt to interpret them as dune limestone. The heights given in the Admiralty Chart may, however, be somewhat exaggerated.

above appear to cover large parts of the continental shelf, where they were exposed when the sea-level was lowered.

Consolidation of the calcareous sand dunes was caused by rain water. Similar processes of consolidation in recent dunes are going on today in many places along the coast.

(3) *Lacustrine and Fluviatile Deposits.*

As has already been mentioned, it is quite possible that some of the lacustrine deposits described in the previous chapter as possibly Tertiary might actually be Pleistocene. In some cases investigations into the micro-fauna or flora of these beds may possibly aid in the determination of their age, but such studies have not yet been undertaken in Western Australia.

The fillings of many lake basins in the North-west, Eastern, Central and South-west Divisions are possibly of Pleistocene age, but little is in general known about these sediments. In the southern part of Lake Cowan, near Norseman, " bituminous " silt and clay have been reported in a bore to a depth of 377 feet below the level of the lake. In some, as in Lake Campion, a mud containing 60% of alunite was deposited. In this connection the " deep leads " of the Western Australian Plateau may be mentioned which were apparently mostly formed after the post-Miocene period of uplift, though probably not all at the same time. Some may even ante-date the Miocene, as, e.g., the Princess Royal deep lead near Norseman, where gold was obtained from below the Miocene sponge spicule sandstones. These occurrences cannot be described in detail in the present paper and it must suffice to refer to published accounts. (Jutson, 1934 ; Clarke, Prider and Teichert, 1944, pp. 285-286).

Small occurrences of marl deposits are known from many places in the South-West Coastal Plain, some of them containing freshwater gastropods though these deposits may be of early Recent origin.

Synopsis of Sedimentary Areas.

Sedimentary sequences reflect the tectonic behaviour of crustal units. They bear witness not only of the tectonic movements of the area of accumulation but also to a certain extent of the behaviour of adjacent land masses that supplied the sediments. From this point of view we arrive at the following classification of sedimentary areas in Western Australia :

(1) Scattered outcrop areas.
(2) Large, comparatively thin sheets of sedimentary rocks.
(3) Coastal basins.
(4) Major sedimentary basins.

(1) *Scattered Outcrop Areas.*

Here are grouped scattered and mostly small areas of sediments resting on a Precambrian basement. Thicknesses measure in hundreds of feet or even less. This is a rather inhomogenous group of outcrop areas which, however, may be considered together here, because they are not of great importance in the general structural set-up of Western Australia.

Firstly, we have outcrops that are remnants of a once larger sheet of sedimentary rocks most of which has been eroded away. Typical examples are the Tertiary sediments on the Precambrian in the southern part of the Western Australian shield (Plantagenet beds, Norseman limestone, etc.) and the many outcrops of sandstones and boulder beds of possibly Cretaceous age (outliers of the Wilkinson Range beds) that are found on the Precambrian shield from the Ponton River in the south to Lake Carnegie in the north, that is roughly over an area of 60,000–70,000 square miles. These sediments are of greatly varying

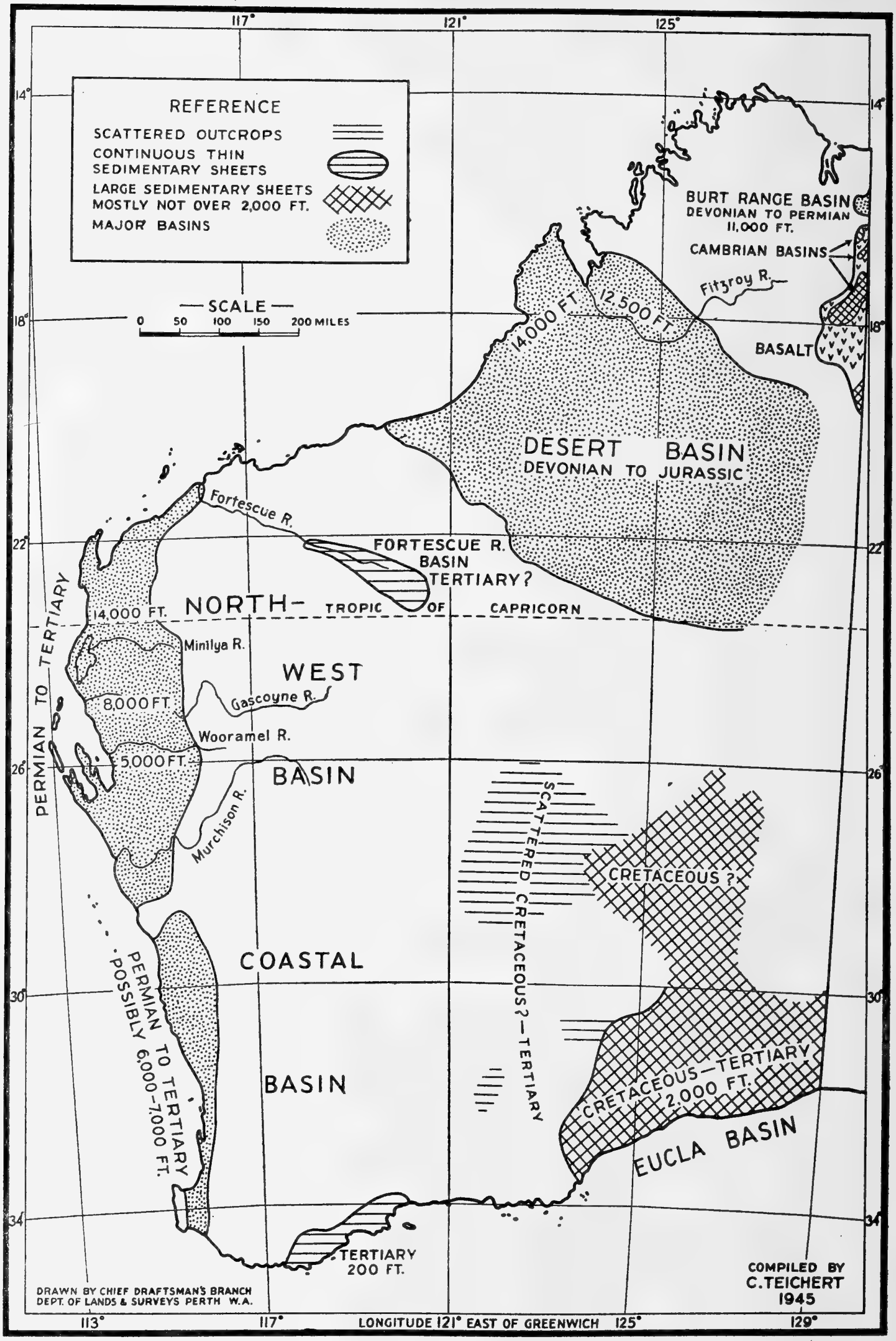

Fig. 8.—The sedimentary areas of Western Australia.

(mostly unknown) thickness which perhaps never greatly exceeds 200 feet. In places the thickness dwindles to a few feet, as in the case of the Miocene limestones on the bed of Lake Cowan. All these sediments are of very great palæogeographical interest, because they indicate short temporary *en bloc* submergences of large portions of the Precambrian shield. Adjacent areas to the east were similarly submerged, but did not rise again to their previous level.

A second category in this group are isolated outcrop areas which have been preserved through downfaulting. There are few examples of this type in Western Australia. The best known is the Collie coal basin in the extreme south-west of the State, about 100 square miles large and entirely surrounded by Precambrian granites. The thickness of the beds here is not exactly known, but must be upwards of 2,000 feet, and the general geological setting suggests that the margins of the basin are faulted. Similar basins might exist in this vicinity. The Collie Basin is situated well inside the Precambrian shield, about 20 miles from its western margin which breaks off in a 700 feet scarp towards the Coastal Plain. Of possibly tectonic origin is also the low country between the western margin of the shield and the ridge of Precambrian rocks that extends between Cape Leeuwin and Cape Naturaliste, and which is underlain in its northern part by at least 1,000 feet of sandstones and shales. However, this area might be a southern continuation of the South-west Coastal Basin.

Last in importance among the scattered outcrop areas are sediments that have been laid down in disconnected basins. There are many of them scattered all over the Western Australian shield, but only few of them are of appreciable size.

The largest no doubt is the Fortescue River basin, with an unknown thickness of possibly Tertiary sandstones. Next in importance are perhaps the sediments of the Oakover River, variously referred to the Permian, Cretaceous, Tertiary and Pleistocene, though very little is actually known about them. The Tertiary (?), Pleistocene and Recent sediments of the many salt lakes of Western Australia are also to be included in this category.

(2) *Sheets.*

These are sediments spread out in large " sheets ", either undisturbed or only slightly deformed. Thicknesses measure up to a few thousand feet, but are small compared to the size of the " sheets ". A typical example are the Cretaceous-Tertiary sediments of the Nullarbor Plain, whose thickness only slightly exceeds 2,000 feet. Here sandstones and shales of Cretaceous age are overlain by the Miocene Eucla limestone. The attitude of the beds over an area of probably more than 25,000 square miles is practically horizontal, probably with an imperceptible dip towards the coast, and with large-scale warpings having an amplitude of several miles and a height of not more than a few feet.

After the formation of the sediments in this area the Precambrian basement remained at such a level that the bulk of the sediments escaped erosion, even if some elevation did take place. A similar area might be that covered by the Wilkinson Range beds farther north, in the interior of the Eastern Division.

To this category also belongs the Cambrian of the East Kimberley Division. Here it is the Lower Cambrian basalt which covers huge tracts (extending into the Northern Territory) like a blanket which has been thrown into broad folds. Remnants of the overlying sedimentary series of Lower and Middle Cambrian age are preserved in the basins, although they are not entirely absent from the domes. This area occupies a somewhat unique position owing to the thick sheet of basalt which is intercalated between the Precambrian below and the sediments above.

(3) *Coastal Basins.*

Narrow coastal strips underlain by an unknown, but probably great thickness of sediments. Known thicknesses are a few thousand feet. The best known example is the South-West Coastal Basin between 33° 40′ and 28° 50′ S. lat. It is almost 350 miles long and from 10 to 30 miles wide. On the east side it is bordered by the western margin of the Great Western Australian Plateau whose gneisses and granites rise rather abruptly to a height of several hundred feet above the coastal plain. In the west the coastal plain merges into the continental shelf which is generally 20–30 miles wide, widening to about 60 miles towards the north and south. Coastal plain and shelf may be regarded as one geological unit, because only very slight variations in sea-level would enlarge either at the expense of the other. Unfortunately little is known of the geology of the continental shelf, except along the coast off Fremantle.

The South-West Coastal Basin contains Permian, Jurassic, Cretaceous, Tertiary and Pleistocene rocks, much of which are concealed under a cover of Recent sand deposits. In several places the strata underlying the Coastal Plain have been pierced by bores down to 2,500 feet and beds of various ages have been met with. Near its northern end the Dongarra and Yardarino bores, traversing sediments down to a depth of 2,100 feet, might have reached Jurassic rocks, but probably did not strike the Permian, which crops out 20 to 30 miles inland. The Moora Bore, 100 miles farther south, penetrated 1,150 feet of Jurassic and continued to a depth of 2,230 feet in what are probably Permian sandstones and shales. Deep bores below Perth have proved the existence of over 2,000 feet of Tertiary and probably Cretaceous sandstones and shales, and on Rottnest Island, 12 miles off the coast in the same latitude, a bore was sunk to a depth of 2,582 feet, this being the only source of information as to the beds underlying the continental shelf. A condensed record of the succession here is as follows:

	Thickness in Feet.
Superficial sand	20
Limestone	210
Sandstone and loose sand	1,075
Sandstone and shale	278
Shale and sandy shale	622
Sandstone and loose sand	273
Shale	174
Total	2,582

The age of these beds is unknown, though must be presumed to be mostly Tertiary, perhaps extending downward into the Cretaceous.

Farther south in the Bunbury area over 1,000 feet of sediments that might be of Permian age were found.

Near the northern end of the Coastal Basin (Irwin River district) Permian strata of over 3,000 feet thickness occur. That this Permian belt once continued in a southern direction is suggested by the existence of the Collie and Wilga coal basins in the south. Its continuation under the Coastal Plain would seem likely even if the Moora Bore log did not suggest it. Thicknesses of the Jurassic as far as known from outcrops certainly exceed 1,000 feet and have been estimated to be as much as 2,000 feet. Cretaceous may not be expected to have exceeded a few hundred feet, but Tertiary, from evidence available from the Perth Bores, must at least locally be thicker than 1,000 feet. A total thickness of between 6,000 and 7,000 feet of sediments below the Coastal Plain and the continental shelf is therefore entirely within the realm of possibilities.

No other structural units which are exactly comparable to the South-west Coastal Basin are known in Western Australia. Conditions might be somewhat similar in the northern extension of the North-west Basin, where the sedimentary belt narrows considerably north of Onslow. At Onslow 1,729 feet of sediments, mostly shales, have been found in a bore. These beds are probably an extension of the Cretaceous from the country farther south. North of Onslow geological conditions are unknown.

(4) *The Major Basins.*

The last and most important class of sedimentary areas in Western Australia are the major basins of many thousand square miles and with thicknesses in excess of 10,000 feet. There are three of them in the State, one of which, the Burt Range Basin, however, is only partly situated on Western Australian territory. It might be well to describe this, the most recently discovered, first.

(*a*) *Burt Range Basin.* Although not comparable in size to the other two basins to be described below, it seems to contain a considerable thickness of sediments, but only the southernmost part of the basin is known at present and even this has only been superficially examined. The section in the vicinity of the Burt Range (near the Northern Territory boundary at about 15° 50′ S. lat.) is as follows:

		Feet.
Permian	Sandstones and conglomerates	1,000+
Carboniferous	Bryozoan limestone	350
Devonian	Sandstone series	1,000
	Fossiliferous limestones, calcareous sandstones and shales.	4,000
	Sandstones and conglomerates (Cockatoo series) ..	4,800
Total	.. ..	11,150+

The area occupied by these rocks on the Western Australian side of the boundary is as far as known at present only a few hundred square miles. However, the country along the boundary north of 15° 40′ has never been geologically examined and from disconnected observations by surveying parties of the Lands Department of Western Australia it seems likely that much, if not all, of this country is underlain by sediments. Many maps showing the distribution of Artesian basins in Australia indicate a "Gulf Basin" in this general vicinity, although I have been unable to discover on what evidence the assumption of this basin could have been based.

North of the Burt Range the sediments strike across the boundary into the Northern Territory in the direction of the Keep River and may continue in that direction as far as the Victoria River. An area of Permian sediments has long been known to exist along the coast between the Victoria and Daly Rivers in the Northern Territory. The fossils suggest beds with close affinities to the Nooncanbah and Wandagee series of Western Australia. It is possible that the Burt Range Basin continues in this general direction and includes this or similar

Permian areas. In this case one would expect that the thickness of the sequence should at least be maintained ; however, at Port Keats and Anson Bay, near the coast between Victoria and Daly Rivers, bores sunk in search for coal went through 1,500 feet of Permian and are said to have struck granite underneath (Jensen, 1918), so that it would seem that the older sediments of the Burt Range section peter out in this direction. A broad regional survey of this area is urgently required. The size of the basin may turn out to be of the order of 15,000 square miles.

(*b*) *Desert Basin.* We now proceed from the almost unknown to the little known. It has already been pointed out that only a comparatively small part of the Desert Basin has been investigated. Its north-eastern marginal regions are best known ; the position of the south-western margin has been more or less fixed but the succession here is practically unknown ; the south-eastern margin has never been seen by geologists and as shown on existing maps, including the ones in the present paper, it is entirely hypothetical. Although the size of the Desert Basin is usually given as about 140,000 square miles, this figure might well be somewhat too small.

In the present state of our knowledge it is, therefore, impossible to indicate thickness, distribution of facies, etc., for the entire basin. Certain possibilities only can be suggested.

We may be sure that the sedimentary sequence of the basin is made up of rocks of Devonian and Permian age ; to these Jurassic rocks may possibly be added. The succession in the northern part of the Basin is as follows :

		Feet.
Permian	Erskine series. Conglomerates, sandstones, shales ..	350
	Upper Ferruginous series. Clays, grits, sandstones..	1,400
	Nooncanbah series. Shales, limestones	1,200
	Lower Ferruginous series. Grits, sandstones, shales..	2,200
	Nura Nura limestone	20
	Various sandstones and boulder beds. Grant Range series, Kungangie series, Willanyie series Up to	2,300
Upper Devonian ..	Reef limestones, passing south-eastward into conglomerates, sandstones, shales of decreasing thickness	Maximum about 5,000
Middle Devonian ..	Reef limestones and brachiopod limestones.	

The maximum thickness of Palæozoic sediments in this part of the basin may thus be as much as 12,500 feet.

Whether or not this thickness is maintained basin-ward is at present entirely a matter of speculation. From observations along the Canning Stock Route in the south-eastern part of the basin it seems that sandstones in a more or less horizontal position underlie much of the interior of the basin, and since the beds in the north-eastern part of the basin dip towards the south-west, that is basin-ward, it may be expected that the sandstones of the interior are rather high in the sequence. This is also borne out by aerial observations in the north-east corner of the basin (Woolnough, 1933). Also in the north-western part of the basin Clapp found evidence of a thick sandstone series along the edge of the interior plateau of the basin. It seems that these sandstones must correspond to the higher parts of the Permian series as known in the vicinity of the Fitzroy River (Liveringa and Erskine series, and perhaps higher) and there is thus every

indication of the existence of a considerable thickness of Palæozoic sediments in the interior of the basin.

What happens to the Devonian in the interior of the basin is at present entirely unknown, though there are indications that the limestone facies, so much in evidence along the north-eastern margin of the basin, might not continue far into the interior. An old artesian bore 67 miles east of Derby and only about eight miles from the limestone scarp of the Napier Range has the following interesting log (greatly condensed from the original):

	Depth in Feet.
Sandstones with very little shale; conglomerates near the base	3–1,059
Fossiliferous limestone	1,059–1,170
Very hard to sandy limestone	1,170–2,131
Sandstone with very little shale	2,131–3,012

The bore first went through 1,059 feet of basal Permian sandstones. Below this level the Devonian was no doubt entered and the "fossiliferous limestone", here about 110 feet thick, must be the *Productella* limestone. At 1,170 feet the bore entered the massive reef limestones of the Upper Devonian and continued in them for 961 feet. The rest of the section (981 feet) is in sandstone which is not known from outcrops in the Napier Range. It is very probably the sandy facies of the Middle Devonian which appears here in the bore.

Nothing more is known about the Devonian nearer the centre of the basin. Permian fossils have been found at No. 27 Well on the Canning Stock Route, only a few miles from the south-western margin of the basin. It is possible that the Devonian is here buried (perhaps downfaulted along the edge of the basin) but it is equally possible that no Devonian exists in this part of the Desert Basin.

Finally, Jurassic beds appear in the stratigraphical column of the north-western part of the basin, towards the coast, where the basin probably deepens appreciably. Below Broome there are at least 500 feet of marine Jurassic shales and sandstones (from approximately 900 to 1,400 feet). The beds between the surface and 900 feet are probably at least partly Jurassic (lacustrine); some of them may be Tertiary. Below 1,400 feet there is an increasingly sandy section down to 1,775 feet which is as deep as the deepest bore has penetrated the sequence. Thus we find post-Palæozoic rocks down to at least 1,400 feet, possibly still deeper. Farther inland the marine Jurassic beds rise closer to the surface; 20 miles south of Derby they occur at not more than 300 to 400 feet below sea-level, although their thickness here is not known. At Derby there seems to be a subsurface section of about 300 feet of lacustrine Jurassic sandstones, underlain by mostly soft sedimentary rocks, apparently mostly shale and sandstone, which have been traversed by the Derby Town Bore to a depth of 2,371 feet. The upper part of this section must be Jurassic, although no fossils have been recovered. Where the Permian begins is at present impossible to say. I have examined fragments of bore cores from a depth of 1,860 feet which contain specimens of a large species of *Cleiothyridina* which is characteristic of the lower part of the *Linoproductus* stage of the Wandagee series of the North-west Basin, though its stratigraphical horizon in the Fitzroy Permian sequence is not known. From general considerations of the correlation of the two basins I should expect this species to occur somewhere near the middle of the Upper Ferruginous series, that is at least 1,000 feet below the top of the Permian, so that the thickness of the Jurassic in the Derby Town bore might thus be between 800 and 900 feet.

If the Palæozoic retains its thickness in the direction of the coastal regions a thickness of sediments in excess of 13,000 feet might be found there.

(c) *North-West Basin.*[18] The sediments of the area known under this name do not shape themselves into a true basin. It would perhaps be more correct to call it a " half-basin " which extends for over 400 miles from the vicinity of the Murchison River in the south northwards as far as Exmouth Gulf and North-West Cape and may continue still farther north as a kind of coastal basin. Structurally the large, but shallow (less than 10 fathoms), embayment of Shark Bay and its southern " appendices " Denham Sound, Freycinet Estuary and Hamelin Pool, must be included in the North-West Basin. It is in this latitude that the basin reaches its greatest width of about 200 miles. The total area underlain by sedimentary rocks is approximately 40,000 square miles. All along its eastern side it is bounded by Precambrian rocks of various ages. It seems that in general conditions of normal stratigraphical overlap prevail along this boundary, although it has not been studied in many places.

The sediments have a westerly dip, though this is only true in a most general way. Actually the strata are undulating and faulted in many places, but structural details are generally not yet well understood. It is true, however, that proceeding from east to west higher portions of the stratigraphical sequence are gradually encountered, the thickness of the section increases, and the greatest thicknesses can be expected generally near the coast, though not necessarily along the coast line itself.

The sedimentary column of the North-West Basin is composed of rocks of Permian, Jurassic, Cretaceous and Tertiary age, and present information seems to indicate that the thickness of the sediments increases from the south towards the north at least as far as 24° S. lat. Beyond that line only the higher parts of the section have been studied.

From disconnected sections in the northern portion of the basin between 22° and 24° S. lat. the sequence shown on the table on p. 131 may be compiled.

The thickness of the Permian seems to decrease southward and at about lat. 25°, along the Gascoyne River, it does not seem to be more than 6,140 feet. The Cretaceous, however, retains its thickness. The Commonwealth Palæontologist, Miss Irene Crespin, has kindly informed me that in the Pelican Hill Bore at Carnarvon she recognizes, from the study of microfossils, Upper Cretaceous mostly chalk, from 170 to 1,105 feet below the surface, and Lower Cretaceous mudstones, glauconitic sandstones and limestones down to 2,000 feet. There are no samples available from between 2,000 and 2,474 feet, but from the official log of the bore I would be inclined to conclude that the top of the Permian is here at 2,307 feet. This would agree with figures to be deduced from the log of the Boolathana No. 4 Bore, 12 miles north of Carnarvon, where the top of the Permian seems to lie 2,290 feet below the surface.

It may thus be expected that in this general vicinity the total thickness of the sediments of the North-west Basin is perhaps not in excess of 8,500 feet.

South of the Gascoyne River the basin widens considerably but much of its width is covered either by the shallow waters of Shark Bay or by Recent

[18] Many artesian bores have been sunk in the North-West Basin, but most of them are percussion bores and samples are available from only a few of these. With nothing but drillers' logs to go on, sub-surface correlation is rendered very difficult as many previous attempts show. For example, as long as it was believed that the Wandagee series was predominantly shaly and formed the top of the Permian sequence, it was usual to " recognize " it in bores just below the Lower Cretaceous, whereas it now appears that the uppermost 1,000 feet of the Wandagee are entirely arenaceous and that at least another 700 feet of sandstones (" Wandagee Hill series ") are found on top of them. It is at present difficult to place those beds that used to be correlated with the Wandagee series " old style ", but they are probably still in the Cretaceous. Similarly, in the southern part of the basin, in the vicinity of Hamelin Pool, it has been customary to regard as Permian the first non-glauconitic sandstone below the Cretaceous greensands and glauconitic clays, at depths of a few hundred feet. The discovery, however, of at least 600 feet of quartz sandstones in the lower part of the Cretaceous section on the Murchison River may necessitate a revision of the principles of bore correlation in that area.

			Feet.
Tertiary		Foraminiferal and coral limestones	700
Upper Cretaceous ..		Bryozoan limestones, greensands, marls and chalk	1,070
Lower Cretaceous ..		Siltstones, cherts and glauconitic sands and clays..	1,100
Jurassic		Quartzose sandstones	25
Permian.	Wandagee series and higher.	Sandstones with increasing intercalations of shale in lower half	3,050
	Cundlego series	Interbedded sandstones and shales..	1,000
	Bulgadoo series	Shales with few sandstone beds	2,200
		Missing link in section.	
	Wooramel and Callytharra series.	Sandstones and calcareous shales and limestones..	850
	Lyons series ..	Sandstones, conglomerates and boulder beds—possibly up to	2,400
	Total ..	.. ..	12,395+

surficial deposits so that it is very difficult to gain an opinion of its structure. Along the Wooramel River (about 25° 40′ S. lat.) the Permian might be no more than 2,800 feet thick. At the same time it has become more arenaceous, shales apparently being quite subordinate in this section. No reliable data are available for any of the younger beds in this latitude. At Gladstone, near the mouth of the Wooramel, 540 feet of shales and clays were found in a bore, but apparently the bottom of the Cretaceous was not reached here. Forty miles to the west on Peron Peninsula, a bore penetrated 1,750 feet of soft rock, mostly clay and shale (possibly including chalk), and from our knowledge of the Cretaceous stratigraphy farther south along the Murchison River it may be concluded that this bore stopped at least 500 feet short of the bottom of the Cretaceous series. With a possible 2,800 feet of Permian rocks underneath, it would seem that even in this part of the basin a minimum thickness of sediments of not less than 5,000 feet may be expected.

South of about 26° S. lat. the contents of the basin are almost entirely unknown, with the exception of 700 feet of Cretaceous sandstones, shales and chalk along the lower course of the Murchison River.

Tectonic Classification of Major Basins.

In this discussion we may perhaps neglect the recently discovered "Burt Range Basin", because too little is known about it at present.

Sedimentary basins of first-class importance are the Desert Basin, the North-West Basin, and possibly the South-West Coastal Basin. As regards the last it is true that many stratigraphical facts are available, but its structure is so little known that no clear picture of it can be given and its classification cannot be attempted.

The Desert Basin and the North-West Basin are not exactly comparable. They differ somewhat in size, shape, structure and in the age of their sediments

and it is well first to concentrate on certain aspects of their sedimentational history.

The Desert Basin of 140,000 square miles seems to be more truly basin-shaped, with upturned beds probably around three of its four sides, but

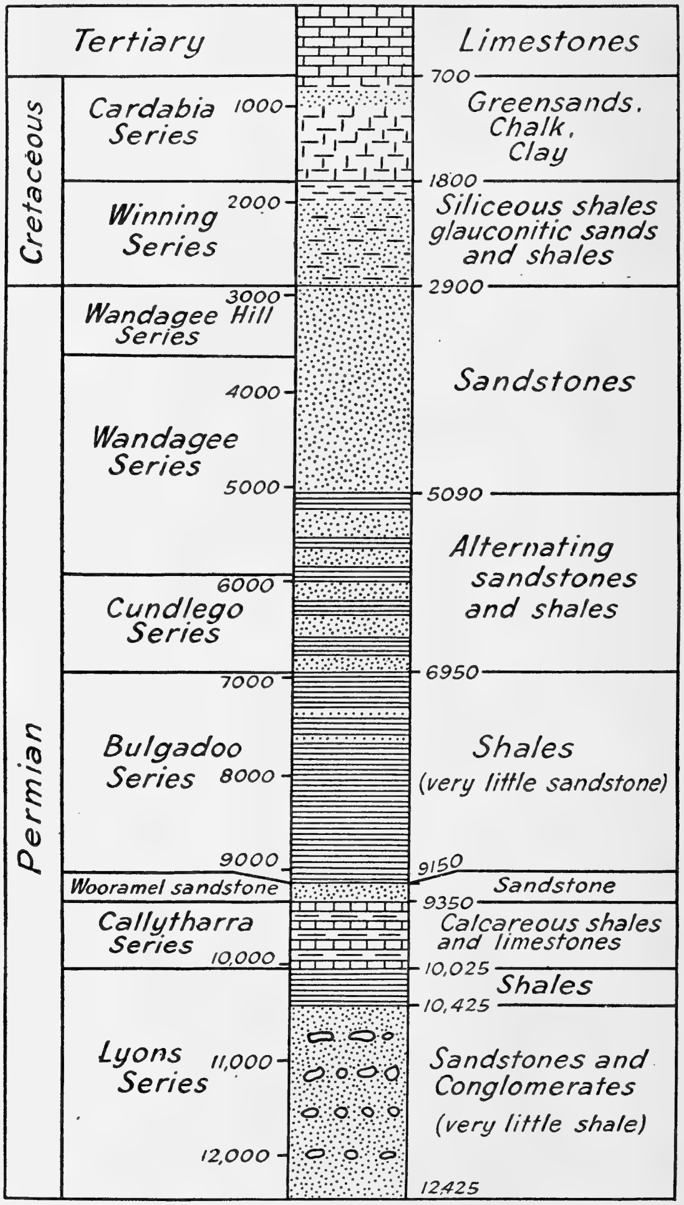

Fig. 9.—Stratigraphical section in the northern part of the North-West Basin. (Jurassic omitted.)

deepening gradually towards the fourth, north-western, side. Near its northern margin it contains at least 12,000 feet of sediments of Middle and Upper Devonian, and Lower to Middle Permian age. Jurassic sediments at least 800 feet thick are present in the north-western part of the basin.

The North-West Basin, as has already been indicated, is an elongated half-basin of some 40,000 square miles in which the strata have a general westerly dip towards the sea, or rather the continental shelf. The maximum thickness of sediments is found in the northern part of the basin, where it may well exceed 14,000 feet. Strata of Lower to Middle Permian age, probably very little Jurassic, and a fair thickness of Lower and Upper Cretaceous, Eocene, Oligocene, Miocene and probably Pliocene, are present. The most remarkable feature of this part of the basin is the thick series (up to 10,000 feet) of Permian shales and sandstones, the bulk of which was deposited in Artinskian time. In the southern part of the basin, as we have seen, the thickness of the sedimentary filling decreases to 5,000 feet or perhaps even less.

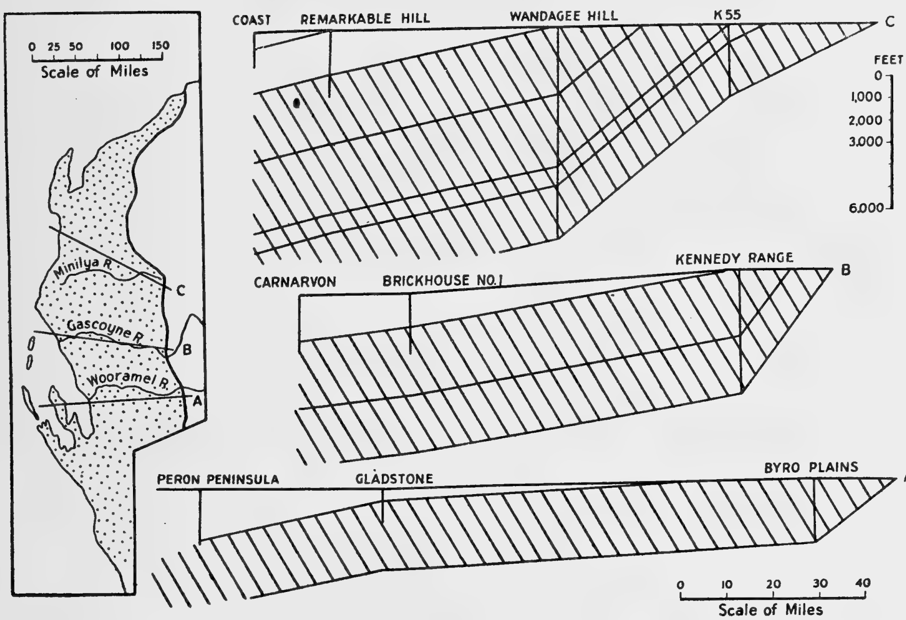

Fig. 10.—Three diagrammatic cross-sections through the North-West Basin, showing decrease in thickness of strata from north to south.

Areas in which sediments have accumulated in such thicknesses are usually called " geosynclines " or " geosynclinal basins ". This conception was first applied to the Desert Basin by Forman (Forman, 1930) and extended to the North-West Basin by Teichert (1939*b*). I then regarded the two basins as parts of one structural unit, the " Westralia Geosyncline ", which, it was suggested, may have formed a southern continuation of the Timor-East Celebes Geosyncline of the East Indies, although the troughs showed marked differences in their depositional and orogenetic history.

There is no need in this place to enter into a discussion of fundamental concepts of geotectonics. Not every geologist would class the Western Australian basins as geosynclines. For example their general features agree well with Tercier's "paralic basins" (Tercier, 1939) of the continental shelves. Tercier describes such basins as intracontinental or pericontinental and their sediments as generally thick, often several thousand metres, predominantly terrigenous, partly marine, partly estuarine and continental. The marine facies is exclusively neritic, characterized by a predominance of detrital rocks, organogenic rocks

being subordinate. They indicate considerable, mostly continuous subsidence. Such series are often found marginal to great mountain ranges, e.g. the molass. Other examples are the Neogene basins of Sumatra, Java and Borneo ; the Gulf Coast basin of North America (Gulf Coast Geosyncline of Russell and others) ; the coal basins of western Europe and eastern North America ; the Old Red deposits of Europe, Spitsbergen and Greenland.

Tercier's paralic basins are at least partly identical with Umbgrove's "idiogeosynclines" or "basin geosynclines" (Umbgrove, 1933). This term he coined for the great oil-producing basins of Tertiary sediments on Sumatra, Java and Borneo which were included by Tercier in his paralic basins. Thicknesses here are up to 20,000 feet, locally even more, and much of the sediments were deposited during the Neogene alone, that is probably in 20 million years or less.

In Western Australian some Permian sequences have accumulated at the rate of 10,000 feet in seven to ten million years. In the East Indian basins sediments did not collect more rapidly.

This interpretation of the North-west and Desert Basins of Western Australia is an alternative to the idea of a Westralian Geosyncline as set forth in 1939.

Obviously these considerations are of more than theoretical interest, because Tercier's paralic basins, or Umbgrove's idiogeosynclines constitute a structural province which is known to contain many important oil fields.

Oil Possibilities.

The practical significance of many of the stratigraphical facts discussed in this paper is self-evident and in the following I shall be satisfied to emphasize a few additional points, mainly structural, which have been inadequately treated in the preceding chapters.

The existence in Western Australia of large areas of sedimentary rocks attracted the attention of the oil industry long before details of the sections were known, but early investigations were often superficial and most later surveys were either of the broad reconnaissance type or they concerned themselves with detailed studies of only portions of the great basins.

South-West Coastal Basin.

Little is known about the structure of the South-west Coastal Basin. The Precambrian escarpment, known as the "Darling Range", which borders it along much of its east side, is very pronounced along the edge of the Coastal Plain south of Perth and for at least 50 miles north of Perth. Farther north it becomes more indistinct. It has been assumed by many that the Darling scarp is a fault, but there is no direct evidence for this assumption and recent investigations by Prider (Prider, 1941) seem to make the assumption of a monoclinal flexure at least plausible ; also it should be remembered that monoclinal coasts adjacent to ancient shields are known from Natal, Mozambique, Greenland and elsewhere.[19]

All the deep bores put down in search of artesian water are situated near the outer edge of the Coastal Plain, with the exception of the Moora bore, 100 miles north of Perth, which is only two and a half miles from the edge of the Precambrian. If this bore, as seems likely, penetrated as far as the Permian beds, it may be assumed that perhaps there are not more than about 4,000 feet of sediments below the bore site. A slope of the Precambrian surface of not more

[19] Interesting examples from various parts of the world will be found in the following papers : H. Cloos, Hebung-Spaltung-Vulkanismus, *Geol. Rundsch.*, Vol. 30, Zwischenheft 4A, 1939, pp. 503-6 ; J. Bourcart, La marge continentale, *Bull. Soc. geol. France* (5), Vol. 8, 1938, pp. 467–71; C. King, Monoclinal Coast in Natal, South Africa, *Jour. Geomorph.*, Vol. 3, 1940, pp. 144–53.

than 16° would be sufficient to bring it down to this depth and the evidence for the existence of a fault along the edge of the Coastal Plain near Moora as suggested by Forman, is therefore quite inconclusive.

Although study of the surface geology is made difficult by extensive covering of Pleistocene and Recent deposits in the Coastal Plain, Forman located an anticlinal structure in presumably Jurassic sandstones at Walyering Peak, west of Moora (Forman, 1935). It is usual to assume a more or less general westerly dip of the strata, but there is not much evidence to support such a simple view and conditions might well be more complicated as suggested by the geological profile west of Moora and by the difficulties experienced in the correlation of the logs of artesian bores at Perth (Forman, 1933).

The question of the nature of the Darling scarp is of obvious significance for the interpretation of the entire coastal basin. If the scarp owes its origin to a monoclinal flexure, this may well be of great age and indicate the position of, or at least run parallel to, former coast lines of the Mesozoic. The conditions may then be present for the existence of up-dip wedge-belts of high porosity which have not hitherto been suspected.

North-West Basin.

In 1925 a well-known oil geologist traversed the North-West Basin and thoroughly condemned it as the most unpromising prospect he had ever had the misfortune to see, his chief reason being that " only a few feet of shale has actually been seen or authentically reported in the Basin ". Ten years later, after Raggatt's survey for Oil Search Limited (Condit, Raggatt and Rudd, 1936), the known thickness of shales in the Permian alone had increased to 2,500 feet, to which another 1,000 feet or so of Cretaceous shales were added. In subsequent years I have myself seen at least 4,000 feet of shale in a narrowly restricted Permian area and present indications are that the combined thicknesses of all Permian and Cretaceous shales in the northern part of the basin must be close on 6,000 feet.

From the point of view of potential source rocks, therefore, the position is satisfactory and the question of porosity and cover seems to find an equally positive answer. There is no scarcity of pervious sandstone, either interbedded with the Permian shales of the Cundlego and lower Wandagee series, or else topping the Permian sequence. More than adequate cover is provided by the impervious clays and marls of the Cretaceous.

These observations have reference to the northern part of the basin only. A number of additional factors entering into the problem have been analysed by Condit (1935) and it may suffice here to refer to his paper.

The North-West Basin is a sufficiently unexplored field in which the search for structures might pay dividends, but much detailed mapping and geophysical prospecting will be necessary. Since I first reported on the existence of large-scale faulting in one part of the basin (Teichert, 1939*a*) faulting has been found to be even more intense. Owing to the almost perfect planation of much of the surface of the basin, such faults are often very difficult to detect on the ground and detailed palæontological zoning work was necessary to recognize them in the field. Aerial reconnaissance will be of considerable value in future work, because structure patterns in flat country are often easily visible from the air.

Anticlines and domes exist in various parts of the basin. Best known is perhaps the Cardabia Range, which is cut out of the western limb of a broad anticline of Cretaceous rocks. Towards the south this anticline probably splits into two or three minor and shallower anticlines and the Cretaceous is covered by Tertiary limestones. Other anticlines which have been known for some time are the Cape Range anticline and the Giralia anticline.

In the Permian belt an anticlinal structure was discovered in 1941 in the Bulgadoo shales, south of the Minilya River and a small dome in strata still lower down in the section is known from the vicinity of Dairy Creek, south of the Gascoyne River. Both these structures are too low down in the sequence to be of any interest to the oil geologist, and the same will probably apply to most other structures in the Permian belt, where considerable thicknesses of strata have been removed by erosion and the highest Permian beds are only found along its western margin.

The young age of these deformations is evident. There is at present no clear evidence for more than one tectonic phase, and this is not older than Pliocene, since Miocene limestone, possibly even Pliocene, have been folded. The youthfulness of the structures is a factor that must be regarded as favourable to the accumulation and preservation of oil.

Permian oil, if it exists, will most probably not be found in the areas of Permian surface outcrops, but farther west where the Permian is covered by Mesozoic and Tertiary sediments. It is, therefore, necessary first of all to obtain an idea of the probable conditions of the concealed Permian sediments in the coastal areas. It will be necessary to establish the maximum thickness of the shales, their exact place in the stratigraphical column, and their geographical distribution. The direction of changes in porosity must be studied. The question of buried hills and of the nature of the contact between the Permian and the Cretaceous (or Jurassic ?) must receive close attention. These and other relevant problems can only be approached on the basis of an integrated picture of the geology of the whole basin. In one section south of the Minilya River I have seen indications of lateral change from shale to sandstone in a westerly direction, conjuring up vistas of borderlands or buried islands. This and the overall westerly dip of the beds suggests possibilities for the presence of porosity belts.

Desert Basin.

Little need be said about the Desert Basin. Six-sevenths of it are unexplored and the stratigraphy of the remaining seventh, the Fitzroy River Basin, has been described on some preceding pages. In the Devonian there is a bewildering variety of facies, including Upper Devonian shales near the north-east corner of the basin. The Permian has thousands of feet of sandstone, but intercalated are shales, particularly in the middle and lower part of the section. The relationships between the Devonian and the Permian have only been incompletely investigated.

From the Fitzroy area Wade (1936) has described a number of structures which he regarded as promising. A bore was commenced in the Nerrima Dome in strata of the Nooncanbah series. It had reached a depth of over 4,000 feet when the war brought about the temporary cessation of boring operations. Earlier bores (Mt. Wynne, Poole Range, Price's Creek) were made after brief reconnaissance surveys only. Their lack of success is not surprising.

The beds in the interior of the basin seem on the whole to have a more or less horizontal attitude, but the true structure of the basin is as yet unknown. Very extensive geological surveys will be necessary before the possibilities of this basin as a whole can be properly assessed.

Conclusion.

From 1938 until 1945 I have spent many months in the field on investigations in all the major and many minor sedimentary areas in the State, with the exception of the inland districts which are still more difficult of access than most of the rest, and I have seen at least parts of all major areas from the air. The costs of most of these travels were defrayed by the Commonwealth

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Acknowledgment must be made of a debt of gratitude to earlier as well as more recent investigators of sedimentary rocks in Western Australia: E. T. Hardmann, A. Gibb Maitland, A. Wade, E. de C. Clarke, F. G. Forman, H. G. Raggatt and others, and to those who pioneered the palæontology of this State: R. Etheridge, Jnr., and F. Chapman, who laid the foundations of systematic palæontology in Western Australia. In my own work I have been ably and unselfishly assisted by many fellow palæontologists. Among those who in recent years have helped in the task of identifying and describing material from the vast palæontological storehouse of Western Australia are: R. S. Bassler (Bryozoa), Irene Crespin (Foraminifera and Bryozoa), H. O. Fletcher (Pelecypoda), Dorothy Hill (corals), Joan Crockford (Bryozoa), B. F. Howell (sponges), W. J. Parr (Foraminifera), J. Pia (Algæ), K. L. Prendergast (Brachiopoda), L. F. Spath (Ammonoids), C. J. Stubberfield (trilobites), A. B. Walkom (plants), F. W. Whitehouse (trilobites), to all of whom I am indebted for advice affecting the correlation of fossiliferous rocks in Western Australia.

It is my desire to place on record my special indebtedness to Professor E. de C. Clarke, Head of the Department of Geology of the University of Western Australia, and to Mr. F. G. Forman, former Government Geologist of Western Australia. Both have proved loyal friends in difficult times and without their confidence and collaboration I could have achieved little in Western Australia.

Much, very much, remains to be done. Large areas of the State which there is every reason to believe are underlain by sedimentary rocks have never been seen by a geologist, and not a single one of even the minor sedimentary areas may be regarded as well known. By European and American standards systematic palæontology which furnishes the basis for all correlation is in a deplorable state in Western Australia. The number of undescribed, new species at present in collections in this State is probably not far from one thousand. Among them are many of the commonest Western Australian fossils. Investigations into the distribution of facies and the sedimentary environment of the major basins, and palæontological zoning, have only just begun. Future researches of this kind are bound to alter many of our present conceptions of the stratigraphy of Western Australia. The present paper, therefore, can be no more than a beginning and a challenge—" but, for the rest, we must partly investigate for ourselves, partly learn from other investigators, and if those who study this subject form an opinion contrary to what we have now stated, we must esteem both parties, indeed, but follow the more accurate" (Aristotle, *Metaphysics*).

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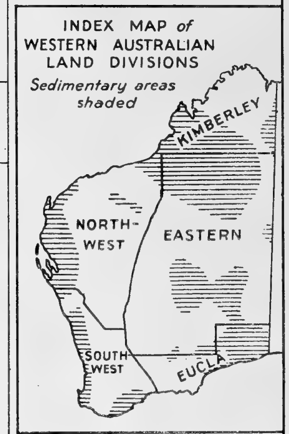
STRATIGRAPHICAL TABLE *of* WESTERN AUSTRALIA

Compiled by CURT TEICHERT

		KIMBERLEY	NORTH-WEST	SOUTH-WEST	EUCLA	EASTERN
		LAND DIVISIONS (*See inset map*)				
Pleistocene		Marine and lacustrine clays		*Marl deposits* of Coastal Plain *Cave deposits* with extinct marsupial fauna	Sedimentary fillings of many dry salt lakes, deep leads, etc., probably date back to this period	
Pleistocene		Deposits of a *Glacial* stage: *Dune limestones* ("Coastal Limestone series") Deposits of an *Interglacial* stage: *Fossiliferous limestones* & calcareous sandstones, emerged *Coral Reefs*				
Pleistocene / Tertiary	Pliocene	Pliocene or early Pleistocene *White Mountain series* Lacustrine cherts, limestones and marls 370 feet	*Pliocene and/or early Pleistocene* Ferruginous and sometimes aluminous hardpan formations known as "laterite" or "duricrust" ? Fortescue River beds (lacustrine)	? Lacustrine sands of Collie basin		
Tertiary	Miocene		Limestones with *Flosculinella* and *Trillina* Limestones with *Lepidocyclina murrayana* and *L. verbeeki* *Aturia* beds of Kennedy Range	*Plantagenet series* Siltstones, sandstones, spongolites 200 ft	*Eucla limestone* of Nullarbor Plain (Possibly partly Oligocene) 900 ft.	*Norseman limestones* and *Lake Cowan spongolites* (up to 50 ft.)
	Oligocene		Limestones with *Lepidocyclina dilatata* and *L. papuanensis*			
	Eocene		*Discocyclina* limestone	Foraminiferal sands and clays in bores below Perth to 770 ft. below sea level		
Cretaceous	Upper		CARDABIA RANGE *Cardabia series* 900 ft. Bryozoa limestone Greensand with *Eubaculites*, etc., Chalk, chalky clay, claystones	MURCHISON RIVER *Murchison House series* 750 ft. Second Gully shale Toolonga chalk Alinga beds Thirindine shale Butte sandstone Tumblagooda sandstone SOUTH-WEST COASTAL PLAIN *Gingin series* Upper greensand Chalk Lower greensand 230 ft.		*Wilkinson Range series* Sandstones, conglomerates, tillites, 200 ft + (possibly of Permian age)
	Lower		*Winning series* 1,100 ft. Siltstones and chert Green gypseous shale Glauconitic sandstone	? Bullsbrook plant beds	Sandstones and shales with *Maccoyella* and *Aucella hughendensis* (in bores only) 1,000 ft.	
Jurassic	Upper	*Derby series* (300 ft) Sandstones with *Thinnfeldia*, *Otozamites*, etc. *Buchia–Belemnopsis* sandstones 500 ft + (in bores only)		*Isoetites* beds of Gingin		
	Middle		*Algal beds* of Minilya River (with *Parachaetetes*) 20 ft.	*Newmarracarra series* Sandstones and shales		
	Lower			*Otozamites sandstones* of Geraldton district and Coastal Plain, 1,000 ft +		
Triassic				? *Donnybrook sandstone* (possibly younger)		

Permian	Middle (Kungurian + Artinskian)	... beds Richly fossiliferous sandstones 1,400 ft. *Noonkanbah series* Richly fossiliferous limestones and shales 1,200 ft *Lower Ferruginous series* Conglomerates, sandstones, shales (*Glossopteris* flora) 2,200 ft *Nura Nura limestone*, marine glacial 20 ft.	? Thick conglomerates and sandstones (insufficiently investigated) ?	Sandstones 700 ft. *Wandagee series* Sandstones and shales 2,350 ft. (d) *Linoproductus* stage (c) *Schizodus* stage (b) *Calceolispongia* stage (a) *Lingula* stage *Cundlego series* Sandstones and shales 1,000 ft. *Bulgadoo shales* 2,200 ft *Wooramel sandstone* 180 ft *Callytharra series* Limestones and shales 675 ft.	*Kennedy sandstone* 500 ft *Byro series* 2,500 ft.	GREENOUGH AND IRWIN RIVERS Sandstones and shales *Irwin River* and *Eradu* coal measures (*Glossopteris* flora) 140 ft. + *Fossil Cliff limestone* 190 ft	*Collie* & *Wilga* coal measures (*Glossopteris* flora) 2,000 ft.		? *Paterson Range series* Permian rocks extend from the West Kimberley into this division (insufficiently investigated) Wilkinson Range series possibly of this age (see under Cretaceous)
	Lower (Sakmarian)	*Grant Range series* *Poole Range series* Sandstones, conglomerates, tillites 2,000 ft. +		*Lyons River series* Sandstones, conglomerates, tillites, 2,000–2,500 ft		Shales and mudstones with *Metalegoceras jacksoni*, 2,500 ft, Tillites 200 ft. +			
Carboniferous			Bryozoan limestone of Burt Range 350 ft.						
Devonian	Upper	Stromatoporoid limestones of Napier Ra., Oscar Ra. etc. abt 5,000 ft *Productella* limestone *Sporadoceras* beds *Cheiloceras* beds *Manticoceras* beds	Sandstones with worm-burrows 1,000 ft Limestone—shale series very fossiliferous 4000 ft *Cockatoo sandstones* & conglomerates (*Lepidodendron*) 4,800 ft.						
	Middle	*Atrypa* limestone *Amphipora* limestone							
	Lower								
Silurian									
Ordovician									Quartzites and sandstones of James Range etc. (Extension of Larapintine series from Central Australia)
Cambrian	Upper ?		*Mt. Elder series* Sandstones 2,000 ft +	? Fossiliferous sandstones overlying Nullagine series					
	Middle		*Negri series* Shales, limestones 1,000 ft. *Xystridurus* zone *Girvanella* limestone *Redlichia* zone						
	Lower		*Basalt* 2,000 ft.						



STRATIGRAPHICAL TABLE *of* WESTERN AUSTRALIA

Compiled by CURT TEICHERT

Period	Epoch	LAND DIVISIONS (See inset map): KIMBERLEY	NORTH-WEST	SOUTH-WEST	EUCLA	EASTERN
Pleistocene		Marine and lacustrine clays		*Marl deposits* of Coastal Plain *Cave deposits* with extinct marsupial fauna	Sedimentary fillings of many dry salt lakes, deep leads, etc. probably date back to this period	
Pleistocene		Deposits of a *Glacial* stage *Dune limestones* ("Coastal Limestone series") Deposits of an *Interglacial* stage *Fossiliferous limestones* & calcareous sandstones, emerged *Coral Reefs*				
Pleistocene		Pliocene or early Pleistocene *White Mountain series* Lacustrine cherts, limestones and marls 370 feet	*Pliocene and/or early Pleistocene* Ferruginous and sometimes aluminous hardpan formations known as "laterite" or "duricrust" ?Fortescue River beds (lacustrine)	?Lacustrine sands of Collie basin		
Tertiary	Pliocene					
Tertiary	Miocene		Limestones with *Flosculinella* and *Trillina* Limestones with *Lepidocyclina murrayana* and *L. verbeeki* *Aturia* beds of Kennedy Range	*Plantagenet series* Siltstones, sandstones, spongolites 200 ft	*Eucla limestone* of Nullarbor Plain (Possibly partly Oligocene) 900 ft	*Norseman limestones* and *Lake Cowan spongolites* (up to 50 ft)
Tertiary	Oligocene		Limestones with *Lepidocyclina dilatata* and *L. papuanensis*			
Tertiary	Eocene		*Discocyclina* limestone	Foraminiferal sands and clays in bores below Perth to 770 ft below sea level		
Cretaceous	Upper		CARDABIA RANGE *Cardabia series* 900 ft Bryozoa limestone Greensand with *Eubaculites*, etc. Chalk, chalky clay claystones MURCHISON RIVER *Murchison House series* 750 ft. Second Gully shale Toolonga chalk Alinga beds Thirindine shale Bulte sandstone Tumblagooda sandstone	SOUTH-WEST COASTAL PLAIN *Gingin series* Upper greensand Chalk Lower greensand 230 ft		*Wilkinson Range series* Sandstones, conglomerates, tillites, 200 ft + (possibly of Permian age)
Cretaceous	Lower		*Winning series* 1,100 ft Siltstones and chert Green gypseous shale Glauconitic sandstone	?Bullsbrook plant beds	Sandstones and shales with *Maccoyella* and *Aucella hughendensis* (in bores only) 1,000 ft	
Jurassic	Upper	*Derby series* (300 ft) Sandstones with *Thinnfeldia*, *Otozamites*, etc. *Buchia–Belemnopsis* sandstones 500 ft + (in bores only)		*Isoetites* beds of Gingin		
Jurassic	Middle		*Algal beds* of Minilya River (with *Parachaetetes*) 20 ft.	*Newmarracarra series* Sandstones and shales		
Jurassic	Lower			*Otozamites sandstones* of Geraldton district and Coastal Plain 1,000 ft + ?Donnybrook sandstone (possibly younger)		
Permian	Middle (Kungurian + Artinskian)	*Upper Ferruginous series* Fusulinid beds Richly fossiliferous sandstones 1,400 ft *Noonkanbah series* Richly fossiliferous limestones and shales 1,200 ft *Lower Ferruginous series* Conglomerates, sandstones, shales (*Glossopteris flora*) 2,200 ft *Nura Nura limestone*, marine glacial 20 ft — ? Thick conglomerates and sandstones (insufficiently investigated) ?	*Wandagee Hill series* Sandstones 700 ft *Wandagee series* Sandstones and shales 2350 ft (d) *Linoproductus* stage (c) *Schizodus* stage (b) *Calceolispongia* stage (a) *Lingula* stage *Cundlego series* Sandstones and shales 1,000 ft *Bulgadoo shales* 2,200 ft *Wooramel sandstone* 180 ft *Callytharra series* Limestones and shales 675 ft — *Kennedy sandstone* 500 ft *Byro series* 2,500 ft.	GREENOUGH AND IRWIN RIVERS Sandstones and shales *Irwin River* and *Eradu* coal measures (*Glossopteris* flora) 140 ft + *Fossil Cliff limestone* 190 ft — *Collie* & *Wilga* coal measures (*Glossopteris* flora) 2,000 ft		? *Paterson Range series* Permian rocks extend from the West Kimberley into this division (insufficiently investigated) Wilkinson Range series possibly of this age (see under Cretaceous)
Permian	Lower (Sakmarian)	*Grant Range series* *Poole Range series* Sandstones, conglomerates, tillites 2000 ft +	*Lyons River series* Sandstones, conglomerates, tillites, 2,000–2,500 ft	Shales and mudstones with *Metalegoceras jacksoni* 2,500 ft Tillites 200 ft +		
Carboniferous		Bryozoan limestone of Burt Range 350 ft				
Devonian	Upper	*Productella* limestone *Sporadoceras* beds *Cheiloceras* beds *Manticoceras* beds Stromatoporoid limestones of Napier Ra Oscar Ra etc. abt 3,000 ft — Sandstones with worm-burrows 1,000 ft Limestone—shale series very fossiliferous 4000 ft *Cockatoo sandstones* & conglomerates (*Lepidodendron*) 4,800 ft				
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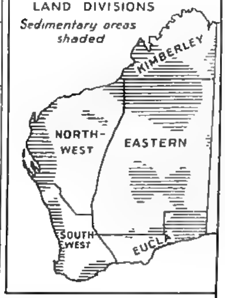
Cambrian	Lower	*Girvanella* limestone *Redlichia* zone *Basalt* 2,000 ft.				

INDEX MAP of WESTERN AUSTRALIAN LAND DIVISIONS

Sedimentary areas shaded



Explanation of Plates.

Plate IV.

Fig. 1.—Vicinity of Mt. Napier, overlooking the flat with Mt. Panton towards the east and north. Rocks in the right foreground are basalt, followed by basal Cambrian limestone steeply dipping north; the low country is occupied by the shales and limestones of the Negri series; Mt. Panton in the distance on the left. Although this country is just outside Western Australia in the Northern Territory the view is typical of basalt and sedimentary topography in the East Kimberley Division.

Fig. 2.—The interior of the Burt Range, showing an anticline in Devonian sandstones and limestones, seen from the southern part of the range looking north. The steep cliff on the right-hand side consists entirely of Permian (?) conglomerates.

Fig. 3.—Upper Devonian conglomerate in bed of tributary of Mt. Pierre Creek, between Mt. Pierre Creek and Trig. Station J 8.

Fig. 4.—Solid stromatoporoid reef weathered out of Upper Devonian shales and sandstones. South-eastern part of Rough Range, West Kimberley Division.

Plate V.

Fig. 1.—South-eastern part of Rough Range with south-west dipping goniatite beds of the Upper Devonian, seen from the south-east; foreground covered with residual boulders of the conglomerate facies of Upper Devonian stage II.

Fig. 2.—Central part of Burt Range. The lower part of the slope consists of Carboniferous limestones, overlain by Permian (?) sandstones and conglomerates. In the foreground Devonian sandstones.

Fig. 3.—Permian sandstones, dipping south, near Gogo Homestead, West Kimberley Division.

Fig. 4.—Calcareous shales and limestones of the Callytharra series. Near Trig. Station K 52 in the northern continuation of the Kennedy Range, between Williambury and Middalya Homesteads, North-West Division.

Fig. 5.—Thin veneer of fossiliferous Miocene limestone on the floor of Lake Cowan, near the "Peninsula", 12 miles north of Norseman. The high ground in the distance is Precambrian of the Western Australian shield.

Fig. 6.—Tertiary limestones of the North-West Cape Range. Yardie Creek.

Plate VI.

Fig. 1.—Aerial view of the country south of the Minilya River, at about 114½° E. long. In the centre of the picture is Wandagee Hill; to the left (east) of it and in the foreground sandstones and shales of the Wandagee series; in the right foreground syncline in upper Wandagee series (beds with *Paragastrioceras, Propinacoceras, Helicoprion,* and rich invertebrate fauna)—this country is shown on Fig. 2. The white cliffs in the distance are shales of the Cretaceous, resting (probably unconformably) on the Permian. The scrub-covered country on the right-hand side is underlain by greensands and shales of the Cretaceous, which are separated from the Permian by a fault. (Photo by permission of the Department of the Army.)

Fig. 2.—Permian sandstones in the North-West Division. In the foreground richly fossiliferous sandstones of the Wandagee series; in the distance Wandagee Hill.

Fig. 3.—Mesa topography on the Irwin River, South-West Division. The cliffs are formed by Permian shales and sandstones.

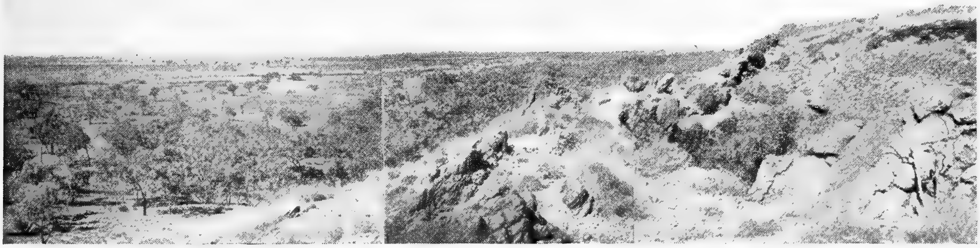
Plate VII.

Fig. 1.—Cliffs of Cretaceous rocks on the north side of the Murchison River, looking south-westward from a point about twelve miles from the shore of the Indian Ocean. The upper part of the scarp is formed by chalk; the lower level is the top of the Tumblagooda sandstone.

Fig. 2.—Cretaceous shales and sandstones of the Cardabia Ranges, looking northward from Remarkable Hill.

Fig. 3.—Emerged Pleistocene coral reef, Pelsart Island, Houtman's Abrolhos. The limestone platform is about 8 feet above mean sea-level; it is overlain by 2–3 feet of non-coralline limestone (in the foreground) and carries a beach ridge of coral shingle of mid-Recent age clearly visible on the platform in the distance.

Fig. 4.—White mountains, East Kimberley Division. In the foreground Pliocene marls and silt stones, capped by chert, dipping 25° N.E. In the distance Cambrian sandstones outcropping at the foot of the hill, overlain disconformably by almost horizontal Pliocene rocks, capped by chert with *Planorbis*.



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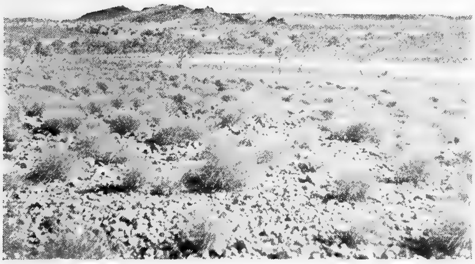

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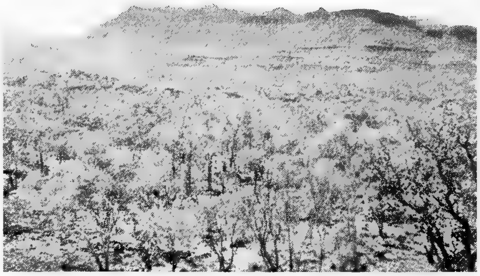

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AN OCCURRENCE OF SYNTHETIC NEPHELINE.

By A. J. Lambeth, B.Sc.

Manuscript received, July 23, 1946. Read, August 7, 1946

During a recent overhaul of one of the glass melting furnaces (No. 8) at the works of Messrs. Australian Glass Manufacturers Pty. Ltd. at Waterloo, Sydney, it was noticed that several of the recuperator tubes were blocked by a non-glassy material, occurring about two-thirds of the way down the tubes. The blocking material was a few feet only in length, and when the tubes were broken open it came away quite cleanly. There were no signs of the material having flowed, and the upper and lower surfaces were almost normal to the face of the refractory.

In hand specimen the material has a uniform greenish grey lithoidal appearance and is quite homogeneous. Under a lens, small milky white blebs in a groundmass are observable, and the general appearance is that of a fine grained phonolite.

Microscopic examination of the thick section showed the presence of phenocrysts in a groundmass. The following characteristics were noted :

Phenocrysts.

Colourless, transparent, as rectangular and hexagonal sections, and also in skeleton crystals in which portions of two or three faces are represented. Hexagonal sections are isotropic, but rectangular sections show parallel extinction and are length fast. Uniaxial, negative ; $\varepsilon=1\cdot538$, $\omega=1\cdot543$ at $24\cdot8°$ C. (Becke oil method). It is concluded that the phenocrysts are nepheline.

Groundmass.

The groundmass has two components, one of which is nepheline similar to that outlined above, occurring in skeleton crystals and plates, and forming a bond, the other component has the following characteristics : green, mostly in grains, some sections prismatic, cross sections are eight sided ; cleavage parallel to the length of the prismatic sections ; pleochroism distinct, greenish brown to yellowish green ; extinction $7°\cdot5$. Length fast ; N_d above $1\cdot7$. It is thought that this material is a type of ægirine ; it is commonly included in a zonal fashion in the nepheline.

A camera lucida drawing of portion of the thin section is given in Fig. 1, in which the phenocrysts of nepheline may be seen in the nepheline-ægirine base.

Discussion.

Attempts were made to separate the minerals for chemical analysis, but although ground to pass 200 mesh, adequate separation could not be obtained owing to the extreme fineness of the ægirine. A sample of nepheline was obtained, however, which although containing appreciable amounts of ægirine was considered sufficiently pure to warrant analysis ; a comparison with the analysis of the original unseparate material is interesting.

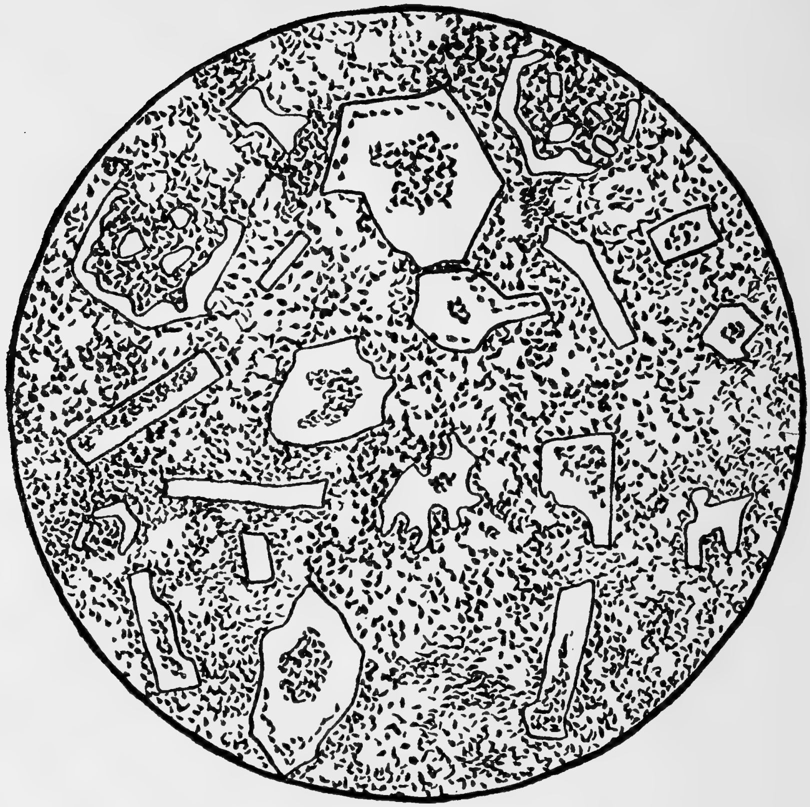

Fig. 1.—Camera lucida drawing (×45) of portion of a thin section of the synthetic nepheline ægirine material. Phenocrysts are nepheline with inclusions of ægirine, stippled is ægirine in a nepheline matrix.

	Nepheline-ægirine Material.	Nepheline Concentrate.
SiO_2	44·79%	42·17%
TiO_2	tr. }	34·74%
Al_2O_3	26·44% }	
Fe_2O_3	9·11%	0·59%
CaO	tr.	0·02%
Na_2O	19·52%	21·50%
K_2O	0·12%	0·18%
P_2O_5	tr.	nd.
	99·98	99·20
	Moisture free basis. True specific gravity : 2·785	Moisture free basis. True specific gravity : 2·65

The specific gravity of the nepheline concentrate (2·65) is slightly above the mean gravity of nepheline as given by Dana (1941), but as the analysis indicates, appreciable quantities of ægirine are present. It would appear that

the composition of the nepheline approaches the composition of the ideal material $NaAlSiO_4$, which requires Na_2O 21·8%, Al_2O_3 35·9%, SiO_2 42·3%.

A computation of the probable chemical composition of the ægirine-like material, from the above analyses, is interesting. It may be assumed that the alumina is entirely bound up in the nepheline molecule. This is indicated by the low extinction angle (7°·5) of the ægirine-like material, which precludes ægirine-augite, augite and similar but alumina-bearing minerals. Consequently the alumina may be used to gauge the amount of soda, potash and silica combined in the nepheline.

	Nepheline-ægirine Material.	Molecular Proportions.	Molecular Proportions of Nepheline.	Remainder.
SiO_2	44·79%	0·746	0·518	0·228
Al_2O_3 ..	26·44%	0·259	0·259	—
Fe_2O_3 ..	9·11%	0·057	—	0·057
Na_2O ..	19·52%	0·315	0·258	0·057
K_2O	0·12%	0·001	0·001	—
		Col. 1	Col. 2	Col. 3

In column 2 are the molecular proportions of the nepheline present, calculated on the assumption that it contains all the alumina and potash. By subtracting the figures given in this column from those in column 1, a remainder, given in column 3, is obtained ; this shows that the second mineral present has the composition $Na_2O . Fe_2O_3 . 4SiO_2$, which is exactly that of ideally pure ægirine.

The material, therefore, consists of nepheline and ægirine in the proportions 259 and 57 by balance, or approximately 82 and 18 per cent. The weight-percentages of the two minerals, obtained by converting the molecular proportions, are 73·6 and 26·4.

The recuperators in which this material was found are fireclay tubes of about one foot diameter, built vertically within a brickwork chamber. The exhaust gases from the furnace pass through these tubes on their way to the stack, while the incoming gases circulate round the tubes in the chamber. The system is thus a type of heat exchanger. The length of the tubes is about twenty feet. During the life of this furnace the exhaust gases were maintained at a temperature of 1900° F. at the point of entry into the recuperator, while at the base of the tubes the temperature had been reduced to 950° F. The temperature within the furnace itself was of the order 2450° F. Once a tube became blocked the temperature within would naturally fall, and it is estimated that the temperature within a closed tube would be 1400° F. maximum, and 950° F. minimum. It would appear therefore that these minerals formed and crystallised within a temperature range of 950° F.–1900° F.

It is to be noted that there was no bond between the blocking material and the tubes ; this was confirmed by micro sections of both materials at the point of contact. The tubes did not contain any visible nepheline or other compound of a foreign nature, and the blocking material contained no mullite or other clay material. It is evident therefore that the tubes played no part in the origin of the minerals under examination.

The glass melted in the furnace was a typical soda lime type; the batch consisted of soda ash, ground limestone and sand. It is known that appreciable quantities of soda ash are lost as "fly" in the gas stream, and this is undoubtedly the origin of the soda in the minerals; the silica may have come from the batch in a similar manner, but this is unlikely because it is known that only very small quantities are lost in this way. Alumina and potash, also, are not likely to have come from the batch, as it is known to have contained only minute quantities of these substances; similarly in the case of iron, as the glass melted was "white" precautions were taken at all times to prevent iron-rich substances from entering the batch. The only other possible source of iron, alumina and silica is fly ash from the gasification of coal in producers which are situated near by. It is known that quantities of fly ash pass over in the gas stream, and occasionally settle out in "dead corners" of the gas system, although fly ash alone is not known to have settled out in the tubes as this material did. Titania, phosphorous pentoxide and lime, traces of which were found, probably had a similar source. It is to be concluded, therefore, that the origin of the materials which formed the nepheline and ægirine of this substance, is soda from the glass batch; silica, alumina and iron from fly ash derived from the combustion of coal. It is noteworthy that the minerals so formed are essentially alkaline in nature, but this is to be expected as the formation took place in an atmosphere which at all times contained an abundance of soda.

The possibility that the reaction took place in the combustion zone of the furnace and thus at a temperature of 2450° F. should not be overlooked, but had this been the case, carnegeite rather than nepheline would have been expected (Dana, 1932).

Summary.

Nepheline and ægirine have been identified as the only products formed by the interaction of soda and the ash from coal, under a set of conditions in which the temperatures are known. It is concluded that formation and crystallization took place between 1900° F. and 950° F. The nepheline occurs as phenocrysts, and as small crystals and plates forming a matrix, enclosing ægirine, which is present as small grains and prisms. The composition of the nepheline approaches the theoretical.

The author wishes to express his thanks to the management of Messrs. Australian Glass Manufacturers Pty. Ltd. for kind permission to present this paper.

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MAJOR SHALLOW EARTHQUAKES, 1909–1911.

By D. J. K. O'Connell, S.J., M.Sc., D.Ph.

Manuscript received, July 18, 1946. Read, August 7, 1946.

The best account of the distribution of shallow earthquakes (i.e. those not more than about 40 km deep) is that given by Gutenberg and Richter (1941, 1945). Comparatively few epicentres have been published for the period prior to 1918, when the International Seismological Summary was started. The recent introduction by Gutenberg and Richter of a satisfactory method of determining the intensity of earthquakes from seismograph records makes it all the more desirable that the statistical material should be as complete as possible. When the writer was reanalysing the early Riverview records in order to study deep focus earthquakes, it seemed worth while extending the survey to include also shallow earthquakes. When this work had been carried as far as the end of 1911, it was learnt that Gutenberg and Richter are engaged on a somewhat similar survey. Consequently it was decided to conclude at this point the work on shallow earthquakes in general, although it is hoped to continue the study of deep focus earthquakes and to carry out certain regional surveys for which the Riverview records are particularly suitable. After consultation with Professor Gutenberg, it was decided to publish the work on shallow earthquakes already completed, as it does not in fact precisely duplicate the work being done by Gutenberg and Richter.

All available seismological bulletins were used, as well as fresh readings of the Riverview records. The material is listed in a previous paper by the writer (1946). One of the objects aimed at was to obtain an estimate of the minimum intensity needed for an earthquake to be recorded usefully on good seismographs all over the world. Accordingly epicentres were determined for all earthquakes that were well recorded at great distances from the epicentre. The epicentres were determined by Gutenberg and Richter's graphical method (1937), as described in the writer's earlier paper (1946). The seismological tables used were those of Jeffreys and Bullen (1940).

The magnitudes of the shocks were determined from the amplitudes of the surface waves at the various stations, using Gutenberg's method (1945*a*). The station corrections given by Gutenberg were applied. Gutenberg's paper (1945*b*), describing the method of determining earthquake magnitudes from the amplitudes of P, PP and S waves, arrived after the work was completed. Comparatively few stations reported ground movements, even of surface waves. Only a minority, in fact, of the stations then operating had seismographs that were adequate for the purpose. The stations most used for magnitude determinations were Apia, Batavia, De Bilt, Göttingen, Granada, Graz, Hamburg, Jena, Osaka, Parc St. Maur, Riverview, Uccle, Vienna and sometimes Baku. Ksara, Manila, Ottawa, Pulkovo, Puy de Dome, Reykjavik, St. Louis, Strassbourg.

Column 3 of the Catalogue contains the origin time in Universal Time (G.M.T. reckoned from midnight). Times that are considered to be less accurate are given to the nearest tenth of a minute.

The epicentres in column 4 are given to the nearest half degree. In column 5 is given the number of stations whose readings were available. This number

Catalogue of Major Shallow Earthquakes

March, 1909, to December, 1911.

No.	Date.		Origin U.T.	Epicentre.		No. of Stations.	Quality.	Mag.	No. of Stations.
	1909		h. m. s.	°	°				
1	Mar.	17	22 53·3	2½ S.	122 E.	—	—	6·9	5
2	Apr.	10	5 27·2	16½ S.	172 W.	36	C	7·0	7
3	,,	10	19 35·3	54 N.	158 E.	32	D	7·1	7
4	,,	25	22 35·9	3½ N.	126 E.	23	C	6·5	8
5	,,	27	12 42 50	2½ S.	145 E.	36	C	7·1	10
6	June	3	18 40·7	2½ S.	101½ E.	38	C	7·5	9
7	,,	8	5 46·7	26½ S.	69½ W.	38	C	7·4	9
8	July	30	10 51 54	16½ N.	100 W.	38	C	7·3	7
9	Aug.	14	6 31·0	35½ N.	135 E.	30	C	6·7	7
10	,,	16	6 58·9	9 N.	92 W.	34	D	6·6	8
11	Oct.	20	23 41·2	28 N.	69 E.	39	C	7·0	9
12	,,	31	10 23·1	13 N.	100 W.	31	C	6·7	5
13	Dec.	9	15 34·0	10 S.	161 E.	39	C	7·0	7
	1910								
14	Jan.	22	8 48·3	68 N.	18½ W.	71	C	7	6
15	Mar.	30	16 55·9	21 S.	169½ E.	57	B	7·0	10
16	May	1	18 30 33	20 S.	169½ E.	55	C	6·8	10
17	,,	22	6 24 08	43½ N.	149½ E.	60	B	6·9	10
18	June	1	5 55 30	20 S.	169½ E.	55	C	6·8	11
19	,,	1	6 48 12	20 S.	169½ E.	27	C	6·6	9
20	,,	16	6 30 35	19½ S.	169½ E.	71	C	7·5	6
21	,,	29	10 45·1	32 S.	175½ W.	54	D	6·9	9
22	,,	29	14 17·5	32 S.	175½ W.	34	D	6·5	9
23	July	29	10 26·6	5½ S.	142 E.	51	B	6·6	9
24	Sept.	7	7 11 13	6½ S.	151 E.	52	B	6·8	9
25	,,	9	1 13 15	50 N.	172½ W.	56	C	6·9	12
26	Nov.	9	6 02·0	15½ S.	166½ E.	73	C	7·5	10
27	,,	10	12 19·9	15 S.	166½ E.	40	C	6·6	11
28	,,	26	4 41 16	14½ S.	167 E.	60	B	7·2	12
29	,,	26	6 13 08	15 S.	166½ E.	14	B	6·6	5
30	Dec.	10	9 26 43	10½ S.	162½ E.	68	B	7·4	14
31	,,	13	11 37 23	7½ S.	29 E.	78	C	7·3	15
32	,,	16	14 44·9	4½ N.	126 E.	75	B	7·5	12
33	,,	16	18 52·5	4½ N.	126 E.	33	C	6·6	11
34	,,	16	23 16·9	4½ N.	126 E.	13	C	5·7	2
35	,,	17	6 21·3	4½ N.	126 E.	9	C	5·6	3
36	,,	18	2 45·1	4½ N.	126 E.	20	C	6·3	12
37	,,	27	18 52·1	4½ N.	126 E.	20	C	6·0	6
	1911								
38	Jan.	3	23 25 50	44 N.	78½ E.	96	C	8·1	10
39	,,	7	2 14·9	10½ N.	140 E.	57	C	7·0	10
40	Feb.	18	18 41·0	38 N.	73½ E.	88	B	7½	15
41	,,	23	11 14·0	26½ N.	129 E.	49	C	6·8	8
42	Mar.	11	3 15·6	4 S.	155 E.	45	C	6·5	10
43	Apr.	18	18 14·5	32 N.	58 E.	66	C	6·4	6
44	June	3	20 21·1	19½ S.	171 E.	39	C	6·4	4
45	,,	7	11 02·8	17½ N.	101 W.	84	C	7·6	13
46	July	12	4 07·7	8 N.	126½ E.	90	C	7·5	10
47	Aug.	16	22 41·3	7 N.	137 E.	86	B	7·8	12
48	Sept.	15	13 10·0	20 S.	70 W.	63	C	7·0	12
49	,,	17	3	Aleutians		59			
50	,,	17	4 23·8	20 S.	70 W.	33	C	6·9	8
51	Oct.	6	10 16 13	18 N.	70½ W.	59	B	6·5	12
52	Dec.	16	19 14 27	17 N.	100½ W.	78	C	7·2	12
53	,,	31	6 07·2	2 S.	139 E.	53	C	6·8	10

gives a rough indication of the intensity of the shock, compared with others in the same region. It provides, however, no measure of the accuracy of the epicentre, partly because of the number of less reliable stations then in operation, partly owing to the varying character of the shocks themselves.

The magnitude on Gutenberg's scale is given in column 6, and in column 7 the number of stations used for determining the magnitude.

The letter in column 8 gives an estimate of the accuracy of the epicentre, according to a scale described by the writer in a previous paper (1946). A indicates a very accurate determination (probable error of a few tenths of a degree) ; B, good (not likely to be in error by more than one degree) ; C, fair ; D, poor. None of the epicentres given here is of quality A, for reasons discussed in the paper just mentioned.

The Catalogue includes all the shallow earthquakes considered to be of major intensity, from the beginning of the Riverview records in the middle of March, 1909, to the end of 1911. The only minor shocks included are numbers 34 to 37, which were aftershocks of the big earthquake of December 16, 1910. There was only one major shock, No. 49, for which a satisfactory epicentre could not be obtained. It is retained in the list for the sake of completeness.

The remaining 48 earthquakes range in intensity from 6·4 to 8·1. The conclusion may be drawn that earthquakes of magnitude 6·4 (or, say, 6½) and greater might be expected to give useful records at extreme distances on the better types of seismographs operating during the period in question. With the more sensitive seismographs introduced since that time it is to be expected that this limiting magnitude would be appreciably lower.

Of the epicentres in the catalogue, numbers 38, 40 and 47 are the only ones that are given in the lists so far published by Gutenberg and Richter (1941, 1945), so that there is not yet sufficient material for a comparison of results.

Acknowledgements.

The writer is much indebted to Professor B. Gutenberg, of the California Institute of Technology, Pasadena, for his encouragement and advice.

Summary.

Epicentres, origin times and magnitudes were determined for all major shallow earthquakes from March, 1909, to the end of 1911, using all available data, with the object of adding to the material available for statistical studies of

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NOTES TO TABLE ON PAGE 148.

1. Epicentre from Visser (1921).
2. Felt in Samoa.
3. Epicentre difficult to determine ; at most stations the early phases were superimposed on the record of a previous shock (mag. 6½).
6. Destructive in Sumatra (Korintji).
7. Destructive in Chili (Chanaral, Copiapo).
8. Destructive in Mexico (Acapulco, Chilpancingo).
9. Destructive in Japan (Lake Biwa).
11. Destructive in Baluchistan.
15. Felt on Loyalty Islands.
17. Felt in Hokkaido.
18. Perhaps deeper than normal.
21. Perhaps slightly deeper than normal.
25. Perhaps 100-150 km deep.
26. Felt strongly in Espiritu Santo Islands (New Hebrides).
39. There is some indication that the depth may be 100 km (with origin time 2^h 15·0), but the evidence is inconclusive.
46. Perhaps slightly deeper than normal. Agusan Valley, Mindanao.
47. Caroline Islands.
49. Double shock. It was found impossible to disentangle the readings sufficiently to get a good epicentre.

earthquakes. It is also shown that shallow earthquakes of magnitude not less than $6\frac{1}{2}$ on the Gutenberg scale are recorded usefully at the most distant stations, on the better types of seismographs operating at that period.

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PLANT PRODUCTS OF NEW ZEALAND.*

By Lindsay H. Briggs, D.Phil., DSc., F.N.Z.I.C., F.R.S.N.Z.

I should first like to express my appreciation of the honour in being invited by the Royal Society of New South Wales to deliver the Liversidge Research Lectures for 1946. This I take not so much as a personal honour but an opportunity of describing on behalf of numerous investigators some of the pioneering work done on plant products in New Zealand. I think the term pioneering is deserved as in most cases the investigators themselves have tramped over the hills and mountains in search of their plants or trees and often carried the material home on their backs. When dealing with essential oils where several hundred pounds of leaves are required, this has meant a great deal of sheer physical effort.

In the terms of the Liversidge Bequest it is suggested that lecturers should indicate the future field of research rather than give a mere review. As it is impossible, however, to indicate further lines of development without stating what has been done, I propose including a review of work already done on the plant products of New Zealand, with suggestions as to future work; where possible some correlation with the chemistry of the flora of New South Wales will be given.

There is no question that the flora of New Zealand is unique and one of the most remarkable known. Despite the small area of New Zealand, it constitutes one of the distinct botanical regions of the world, equal in importance to regions of much vaster area. No less than 75% of the 1,800 species occur endemic to the country, and the peculiar geography of New Zealand has allowed for the existence of manifold types, tropical to sub-antarctic, sea-level to alpine, desert to rain-forest types. Just as New Zealand offers great scope for the botanist, it offers an almost unrivalled field to the chemist interested in the various constituents found in plants.

So far only a very small number of plants have been chemically studied, and they have yielded diverse types of products, essential oils, alkaloids, colouring matters and dye-stuffs, steroids, tannins, etc. It must be emphasised at the outset that a great deal of this work has been done from purely scientific motives leaving the commercial development, if any, to future investigators.

Several of these investigations have arisen from the discovery of chemical substances of various types in related species abroad and from their economic and medicinal use by the Maoris and early settlers. Elsdon Best, an eminent authority on Maori history, has pointed out that plants were used by the Maoris for medicinal purposes only after the arrival of the pakeha. Before this, the Maori considered his ailments were the punishment of the gods for his transgressions and his fatalist nature did not allow of any appeal to medicine to ease his pain or ward off death.

A list of plants used in the native pharmacopœia is given by Taylor (1867), the medicinal properties of some New Zealand plants by Baker (1886), while Goldie (1904) gives a further comprehensive account of the diseases and remedies of the Maori. A later list of definitely poisonous plants and other possibly

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* Liversidge Research Lectures delivered before the Royal Society of N.S.W., August 12th and 13th, 1946.

medicinal plants was compiled by Aston (1918*a*, 1919*a*, 1923*b*), while additional notes on the chemistry of the flora have been recorded by Gardner (1923, 1924*a*).

In the intervening twenty years since the last summary, a considerable amount of work has been done on the chemistry of New Zealand plants by workers in the universities and government research institutions, and it is the object of the lecturer to summarise the important contributions made in this period. It will be more convenient, perhaps, to discuss them according to the chemical type of compound contained in them rather than from a systematic botanical point of view.

Essential Oils.

Filices.

Recent work has provided further examples of the occurrence of volatile oils in this large class of sub-kingdom.

Pæsia scaberula, "Scented Fern".

This fern, which is common on waste land frequently after a burn, gives a volatile oil only during its fresh growth. An examination of the oil on a small scale (Briggs and Sutherland, 1946) has shown the presence of the paraffin, heptacosane, $C_{27}H_{56}$, while sesquiterpenes are probably also present.

Asplenium lamprophyllum.*

The freshly broken stalks give an immediate odour of oil of wintergreen which has been confirmed chemically (Briggs and Taylor, 1946). The methyl salicylate occurs in the free state and not bound as its glycoside, monotropitoside (Klein, 1932, p. 821). The closely related species, *A. bulbiferum**, is free from this constituent, the detection of whose characteristic odour may thus be used for the identification.

Pinaceæ.*

Agathis australis, "Kauri".

This is one of the most magnificent trees grown, but so much demand has been made for its timber that it is now very scarce except in reserves. The fresh gum and particularly the fossil gum is extremely valuable in the paint and lacquer industry, and gum to the value of over £23,000,000 has already been exported. The essential oil of the leaves of this one endemic species has been examined by Hosking (1928, 1930), who isolated α-pinene, camphene, limonene, citronellal, cineole, borneol, bornyl acetate, cadinene and the diterpene, kaurene. Kaurene is probably related to isophyllocladene which may be regarded as the basic diterpene.

Kauri gum has also been analysed by Hosking (1929), who isolated α-pinene, dipentene and fenchyl alcohol from the steam volatile portion. The presence of glucose, galactose and arabinose was indicated in the gum fraction, while the resin fraction yielded two resin acids and large quantities of neutral kauro-resin, regarded as a diterpenoid oxide. The resin acids will be discussed later.

Libocedrus bidwillii.

From the investigations of Goudie (1923*a*), Birrell (1932) and Hassall, Slater and co-workers (1946), the oil has been shown to contain α- and β-pinene, limonene, a new terpene ketone and a non-diterpenoid hydrocarbon, $C_{16}H_{32-34}$.

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* An asterisk placed after the family, genus or species name indicates that the same family, genus or species respectively is also recorded in New South Wales.

TAXACEÆ.*

Species of the *Podocarpus** genus comprise a large section of the milling timber in New Zealand, the main members of which have been examined for essential oils, the constituents being recorded in Table 1.

TABLE I.

P. spicatus.[1] "Matai."	*P. ferrugineus.*[2] "Miro."	*P. totara.*[3] "Totara."	*P. dacrydioides.*[4] "Kahikatea."	*P. hallii.*[5]
α-Pinene.	α-Pinene.	α-Pinene.	α-Pinene.	
β-Pinene.		β-Pinene.	β-Pinene.	
Limonene.	Limonene.	Terpene alcohol.		
Herabolene ?	Cineole.			
Cadinene.	Cadinene.	Cadinene.	Sesquiterpene.	
Sesquiterpene ketone.		Sesquiterpene Alcohol.	Sesquiterpene Alcohol.	
Podocarprene.	Mirene.	Totarene.	Diterpenes ?	Phyllocladene.
Liquid diterpene.		Rimuene.		

[1] Butler and Holloway, 1939.
[2] Hosking and Short, 1928; Hosking, 1930.
[3] Aitken, 1929; Beath, 1933.
[4] Aitken, 1929; Hunter, 1932.
[5] Briggs, 1940.

The most characteristic feature is the occurrence of diterpenes throughout, often in high yield, each species giving a different isomer. *P. hallii* has been classified as a variety of *P. totara*, but the isolation of a distinct diterpene would support its status as a true species. The genus *Podocarpus* extends to Australia, Africa and Malay and further research is warranted even from a phytochemical point of view. No species from New South Wales has yet been investigated.

Dacrydium Species.

Members of this genus also comprise a large section of the forest trees of New Zealand, and as a further example of the unique botany of this country this genus also includes the world's smallest pine, *D. laxifolium*, sometimes only three inches high at mature growth. The essential oils examined are listed in Table II.

TABLE II.

D. kirkii.[1]	*D. cupressinum.*[2] "Rimu."	*D. biforme.*[3]	*D. colensoi.*[4]
α-Pinene.	α-Pinene.	Terpene.	Terpene ?
Myrcene.			
Limonene.			
Carvone.			
Bornyl acetate.			
Cadinene.	Sesquiterpene.	Cadinene.	Sesquiterpenes.
Sesquiterpene alcohol, $C_{15}H_{25}OH$.			
Phyllocladene.	Rimuene.	Phyllocladene.	Phyllocladene.
Six other unidentified constituents in small amount.	Diterpene.		

[1] Briggs and Taylor, 1946.
[2] McDowall and Finlay, 1925; Carrie, 1932.
[3] Goudie, 1923*b*; Aitken, 1928*a*.
[4] Blackie, 1929, 1930.

The separation of 14 different constituents in the oil of *D. kirkii* using an efficient fractionating column would suggest that a similar reinvestigation of other species would likewise show a much larger number of constituents and add to our knowledge of phytochemistry.

By extracting the woods of Dacrydium species, Hosking and Brandt (1934, 1935, 1936*a*, *b*, *c*) have obtained a very interesting series of related oxygenated diterpenes which will be discussed later.

Phyllocladus Species.

Phyllocladus alpinus.

The diterpene phyllocladene is the main constituent of this oil which has not yet been thoroughly investigated (Briggs, 1937*a*, *b*; Brandt, 1938).

Phyllocladus trichomanoides, " Tanekaha ".

Numerous constituents have been found in this oil, including α-pinene, myrcene, limonene, cadinene, copæne, cadinol, phyllocladene and isophyllocladene (Briggs and Sutherland, 1946). The remaining species, *P. glaucus*, also yields an oil which has yet to be investigated.

Although the genus *Phyllocladus* extends to Tasmania, no member has been listed from New South Wales.

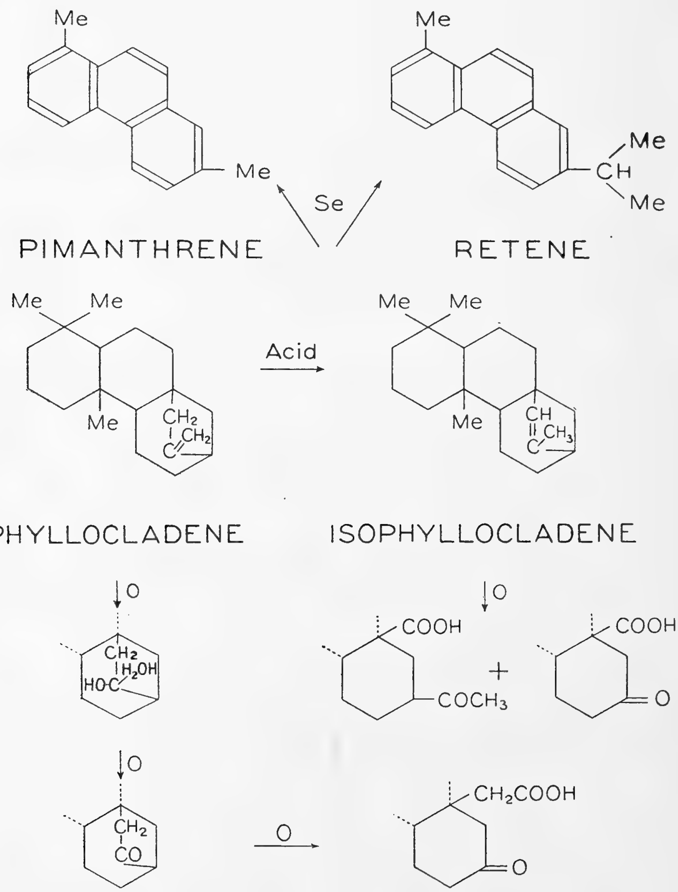


Fig. 1.

The main characteristic of the essential oils of the Pinaceæ and Taxaceæ so far described is the presence of diterpenes, which have already been reviewed by Briggs (1937*c*). The basic compound appears to be isophyllocladene, into which a number of the others appear to be isomerised (see also Briggs and Sutherland, 1942). There are eight possible stereoisomers as well as optical isomers of the tetracyclic isophyllocladene and phyllocladene and a number of the isomeric diterpenes so far described may differ only as stereoisomerides. More diterpenes have been described from the New Zealand flora than from any other source.

Nishida and Uota (1935, 1936) suggested formulæ for phyllocladene and isophyllocladene based on the dehydrogenation to a supposedly new phenanthrene hydrocarbon, " scianthrene ", regarded as 1-isopropyl-7-methylphenanthrene. A synthesis of the latter by Orcutt and Bogert (1941), however, indicated the incorrectness of this view. Brandt (1938), on the other hand, obtained both pimanthrene and retene on selenium dehydrogenation and proposed alternative partial formulæ for these isomers. The criticism by the author (1941*b*), however, that they did not obey the isoprene rule, is invalid and the correctness of these formulæ now appears to be confirmed by later unpublished work of Brandt (1946). (See Fig. I.)

The occurrence of diterpenes in essential oils has been used by Holloway (1938) for a suggested revision of the botanical classification of the families containing them.

PIPERACEÆ.*

Macropiper excelsum.

The one New Zealand representative has been shown (Briggs, 1941*a*) to contain myristicin as its major constituent as well as other unidentified constituents and further work is in progress. The use of this plant as a " pain-killer " for toothache and the isolation of myristicin is interesting in view of the relation of the latter to eugenol, the major constituent of oil of cloves, which is used for the same purpose.

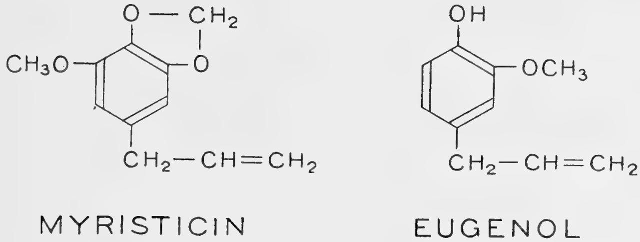


Fig. 2.

MAGNOLIACEÆ.*

Drimys colorata*, " Horopito ".

Melville and Levi (1932) identified in this oil β-pinene, limonene, terpene alcohols, sesquiterpenes and a solid sesquiterpene alcohol. No constituent of the essential oil had the hot taste characteristic of this species.

PITTOSPORACEÆ.*

Pittosporum eugenioides.*

The interesting feature of this oil (Murray, 1946) is that the major constituent (70%) appears to be n-nonane. The other constituents are as yet

unidentified. The fruit of species from the Philippine Islands, e.g. *P. resinifolium* and possibly *P. pentrandrum*, also contain the paraffin, heptane (Bacon, 1909).

RUTACEÆ.*

Phebalium nudum.*

This sweetly scented shrub contains an essential oil investigated by Radcliffe and Short (1928) and found to contain citronellal, citral, cinnamic acid, a phenol, camphene, limonene, a sesquiterpene and a sesquiterpene alcohol.

Melicope ternata.*

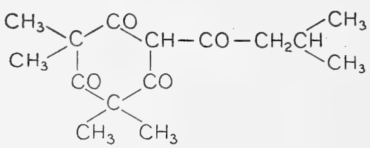
This is one of the most pleasant smelling trees of the flora, but the oil was obtained by Radcliffe (1929) on too small a scale to be investigated in detail.

MYRTACEÆ*.

*Leptospermum scoparium**, " Manuka ".

The constituents of the oil of this species, which also extends to Tasmania and Australia, are highly oxygenated. Besides the terpene hydrocarbons α-pinene, eudesmene and aromadendrene there occur citronellal, citronellol, citral, geraniol, cineole, the phloroglucinol derivative, leptospermone, and acetic, isovaleric and cinnamic acids (Gardner, 1924*b*, 1925 ; Short, 1926).

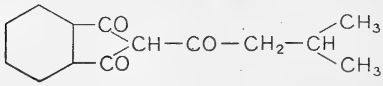
Manuka is probably the most widespread tree or shrub of the flora and its essential oil is probably the most valuable, although it has not yet been used commercially. The oil is very pleasant smelling and could well be used as a cheap perfume for soaps, etc. The unusual constituent leptospermone has been shown (Briggs, Penfold and Short, 1938 ; Briggs, Hassall and Short, 1945) to have the following constitution :



LEPTOSPERMONE

Fig. 3.

and like the closely related constituents from male fern, a well-known anthelmintic, it, too, has anthelmintic properties. It is also closely related to synthetic 1 : 3-indandiones such as " valone ", with high insecticidal properties (Kilgore, Ford and Wolfe, 1942), and tests on the insecticidal properties of leptospermone have shown it to have a good synergistic effect but inferior to valone (Kerr, 1946).



VALONE

Fig. 4.

Leptospermum ericoides.*

This species is not as common as *L. scoparium*. Short and Johnson (1923) have reported the following constituents in the oil, α- and β-pinene, citral, α-terpineol, terpinyl acetate, tasmanol and aromadendrene.

Metrosideros Species*

A survey of the oils from species of this genus (*Metrosideros scandens, M. parkinsonii, M. diffusa, M. colensoi, M. excelsa, M. collina, M. umbellata, M. robusta, M. perforata*) has been made by Gardner (1931). The oils fall into two classes, (*a*) oils containing mainly sesquiterpenes and sesquiterpene alcohols, (*b*) oils containing, in addition to sesquiterpenes and sesquiterpene alcohols, notable proportions of terpenes and terpene alcohols mainly as esters. The terpenes found were α- and β-pinene and dipentene, the ester citronellyl acetate. The sesquiterpene yields cadinene hydrochloride, but attempts to dehydrogenate it to cadalene were unsuccessful, only azulene being isolated. It would appear, therefore, that a mixture of sesquiterpenes is present.

Myrtus bullata.*

A preliminary examination of the oil of this species by Brandt (1946) has revealed the presence of phenols and a crystalline benzoate, $C_{12}H_{12}O_2$, m.p. 68°.

MYOPORACEÆ*.

Myoporum lætum*, " Ngaio ".

The oil from this tree is unique in that there is a complete absence of normal terpene compounds. Besides a solid paraffin, $C_{32-34}H_{66-70}$, 86% of the oil consists of an unusual constituent, ngaione, $C_{15}H_{22}O_3$. Following the original investigations by McDowall (1925, 1927, 1928), Brandt and co-workers (1946) have shown it to have the partial formulæ

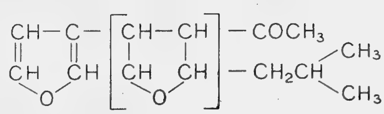


Fig. 5.

The leaves are toxic to sheep and the essential oil has similar toxic properties (Cunningham and Hopkirk, 1945). The Australian species *Myoporum deserti*, " Dogwood Poison Bush ", also has poisonous properties, and an examination of this tree would be of interest.

RUBIACEÆ*.

Coprosma fœtidissima.*

The disgustingly fœtid odour of this plant has been shown by Sutherland (1946) to be due to traces of methyl mercaptan.

COMPOSITÆ*.

Olearia paniculata.*

McLean and Slater (1945) have isolated from the essential oil, β-pinene, limonene, two sesquiterpenes and a diterpene oxide, olearyl oxide, $C_{20}H_{34}O$. The most unusual feature of this oil is the occurrence of a diterpene derivative. Diterpenes are rare in essential oils and occur typically only in the Pinaceæ and Taxaceæ. The presence of such a constituent in a species of the flowering order Compositæ might indicate a more widespread distribution than at present recognised.

Olearia ilicifolia.*

This gives a small yield of oil containing a paraffin alcohol and other constituents still under investigation (Murray, 1946).

CORIARIACEÆ.

Coriaria ruscifolia, C. thymifolia and *C. angustissima.*

Although non-volatile, it is convenient to consider a toxic compound from these species in this section.

From the leaves and seeds of these three species Easterfield and Aston (1901) isolated an extremely poisonous substance, tutin, $C_{15}H_{18}O_6$, closely related to coriamyrtin, $C_{15}H_{18}O_5$ (from the European species, *C. myrtifolia*), picrotoxinin, $C_{15}H_{18}O_6$, and picrotin, $C_{15}H_{18}O_7$ (from members of the tropical family Menispermaceæ*) and iso- and hyenanchin, $C_{15}H_{18}O_7$ (from the African species *Hyenanche globosa*). Japanese workers (Kinoshita, 1930, 1931; Kariyone and Sato, 1930, 1931) regard tutin as identical with " coriarine " from *Coriaria japonica,* since no depression of melting point occurs on admixture and the crystalline forms are identical. Although Slater (1943) regards tutin as different from "coriarine" from differences in the melting point of the acetate and dihydro derivative, the evidence is unconvincing. Little constitutional work has yet been done on tutin, but from its similarity to coriamyrtin and picrotoxinin both chemically and pharmacologically, it would appear that it is not glucosidic as suggested by Easterfield and Aston but an oxygenated lactone of the sesquiterpene series. Since the lethal dose for cats is 1 mg. per kg. bodyweight, while 1 mg. causes nausea, vomiting and incapacity for work for 24 hours in a healthy full-grown man, further work could add considerably to our knowledge of the relation of chemical constitution to physiological activity.

It is of interest to record in this connection that Sutherland (1946) has traced the cause of poisoned honey to this source. Sporadic outbreaks of food poisoning occur in New Zealand which may be traced to the use of honey from certain areas. Suspecting tutin as a possible cause, Sutherland was able to isolate from the poisonous honey in 0·01% yield a new compound, mellitoxin, $C_{15}H_{18}O_7$, obviously related to tutin and of the same order of toxicity. Examination of various parts of the plant of *Coriaria ruscifolia* failed to detect this compound. However, by extraction of the " honey dew ", produced on the leaves at certain seasons by the Passion Vine hopper, *Scolypopa australis,* the same substance was isolated. It is obviously an oxidation product of tutin produced by the insect. Like tutin, it is an unsaturated, hydroxylated lactone probably derived from a sesquiterpene.

The same insect, as well as the native longhorn beetle, *Æmona hirta,* is also responsible for the formation on *Leptospermum scoparium* of a manna, a complex sugar giving only glucose on hydrolysis (Worley, 1928, 1929).

In my opinion a great field still lies ahead in terpene chemistry. Physical methods of analysis such as mass-spectra and infra-red spectroscopy have yet to be applied as general methods. These, however, depend mainly on the constants of known compounds and so far very few terpene compounds have been obtained in a really pure state. Their separation has previously depended on fractional distillation and only in the past few years has any attempt been made to use efficient fractionating apparatus, up to 100 theoretical plates, and most of the work already done on the analysis of essential oils would bear repetition with modern equipment. Fractionation alone is not the whole solution owing to polymerisation and condensation that occurs during the long period of distillation essential in modern practice. It seems obvious from the literature also that, where so-called pure fractions give poor yields of derivatives, these in many cases are mixtures, possibly azeotropes. The use of high-boiling, water-soluble polyhydric alcohols in the formation of azeotropes from which the alcohols may then be removed by solution in water has been used to great advantage in the separation of different types of hydrocarbons in petroleum (Mair, Glasgow, Jr., and Rossini, 1941) and these or similar methods have yet to be applied to the separation of essential oil constituents.

A great deal of knowledge is still required of the chemistry of the terpene compounds themselves. The constitution of a large number of compounds still requires elucidation and those of the diterpenes particularly remain essentially a New Zealand problem. Synthetic work has lagged behind the constitutional side and as an example it may be pointed out that the most common terpene constituent, α-pinene, was only synthesised a few years ago by Komppa.

Comparatively little has been done in the synthetic field using terpene constituents as raw materials, α-pinene being one of the cheapest of chemicals. Just as aliphatic chemistry has been reborn in America and elsewhere in the rise of the petroleum industry, so I suggest that terpene chemistry should be reborn. Most of the terpenes have an initial advantage in being optically active and by the introduction of hetero atoms, oxygen, nitrogen, sulphur, etc., a wide diversity of products could be obtained and exploited.

Resin Acids and Resinols.

PINACEÆ.

Agathis australis, " Kauri ".

Kauri gum has been analysed by Hosking (1929) and among other terpene constituents and resenes (compounds of unknown structure but probably diterpenoid ethers since they give retene on dehydrogenation) a resin acid, agathic dicarboxylic acid, has been isolated. Further investigations by Ruzicka, Hosking and co-workers (1929, 1930, 1931, 1932, 1938, 1941) have indicated the following probable structures for it and its isomeric acid obtained by treatment with acids.

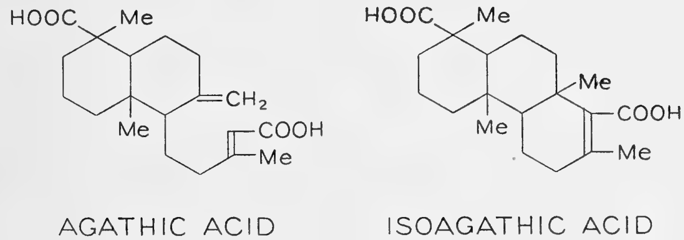


Fig. 6.

These acids differ in their carbon skeleton from the abietic acid type, but have the same carbon skeleton as vitamin A and phytol, the alcoholic component of chlorophyll and vitamins E and K.

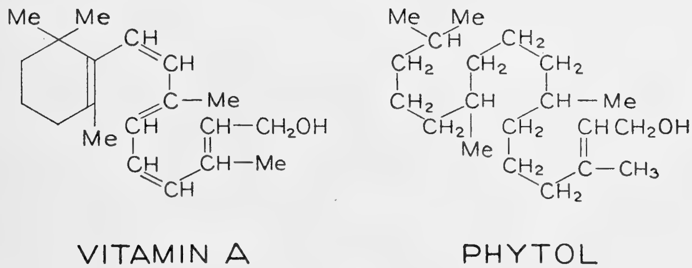
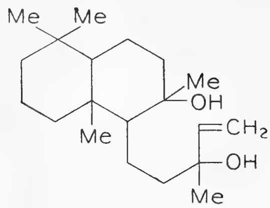


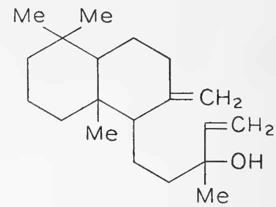
Fig. 7.

Similar compounds occur in the wood of Dacrydium species investigated by Hosking and Brandt (1934, 1935, 1936*a*, *b*, *c*) which in turn are related to

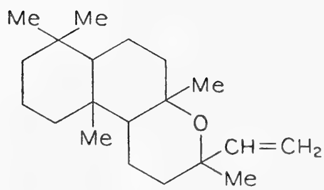
sclareol, a ditertiary alcohol from the oil of *Salvia sclarea* (Janot, 1930, 1931, 1932). The occurrence of these diterpenoid compounds in such widely differing plant families, Taxaceæ and Labiatæ respectively, is worthy of note, while recently a compound of the same type, olearyl oxide, has been isolated by McLean and Slater (1945) from the oil of *Olearia paniculata*, a member of the Compositæ.



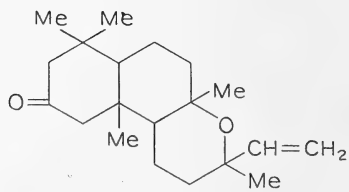
SCLAREOL



MANOOL
(Ex D. BIFORME)



MANOYL OXIDE
(Ex D. COLENSOI)



3-KETOMANOYL OXIDE
(Ex D. COLENSOI)

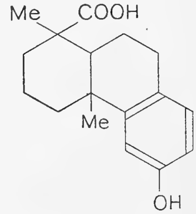
Fig. 8.

The first three substances represent the diterpene analogues of terpin hydrate, α-terpineol and cineole.

That olearyl oxide is related is indicated by the fact that it is dehydrogenated by selenium to agathalene (1 : 2 : 5-trimethylnaphthalene), the aromatic hydrocarbon common to compounds of this series.

A further trihydroxy diterpene oxide from *D. colensoi* apparently belongs to a different series since it yields pimanthrene on selenium dehydrogenation.

From the heartshakes of *Podocarpus dacrydioides*, "kahikatea", and *Dacrydium cupressinum*, "rimu", a resin acid has been isolated by Easterfield and Aston (1903) and identified by Easterfield (1910) as podocarpic acid. Its constitution has been established by Short and co-workers (1933, 1935, 1936, 1938) and Campbell and Todd (1942) as

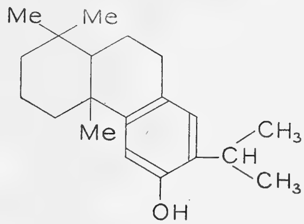


PODOCARPIC ACID

Fig. 9.

which is thus related to abietic acid. As a phenol it has shown some promise as an antioxidant in fats (Brooker, 1946).

The oleo-resin of *Podocarpus ferrugineus*, " miro ", gives rise to ferruginol (Easterfield, 1910), the constitution of which has been established by Brandt and Neubauer (1939) and Campbell and Todd (1940, 1942). It is closely related to hinokiol, $C_{20}H_{30}O_2$, from *Chamæcyparis obtusa* (Yoshiki and Ishiguro, 1933; Keimatsu and Ishiguro, 1935; Huzii and Tikamori, 1939) since both give the same phenol on dehydrogenation.



FERRUGINOL

Fig. 10.

The constitutions of other diterpene acids from this tree (Brandt and Neubauer, 1940) still await elucidation.

The " bloom " of freshly cut totara timber, "*Podocarpus totara*", consists essentially of totarol, $C_{20}H_{30}O$, first isolated by Easterfield (1910; see also Easterfield and McDowell, 1915). Short and Stromberg (1937) have shown it to be a tricyclic secondary alcohol with three double bonds. Dehydrogenation with selenium affords 7-hydroxy-1-methylphenanthrene, but additional work still leaves the constitution doubtful.

There is considerable scope in this field not only on the degradative and synthetic side but in the use of these compounds, especially podocarpic acid with a preformed " aromatic ring ", for the preparation of useful therapeutics. As an example, Fieser and Campbell (1939) have by simple reactions transformed

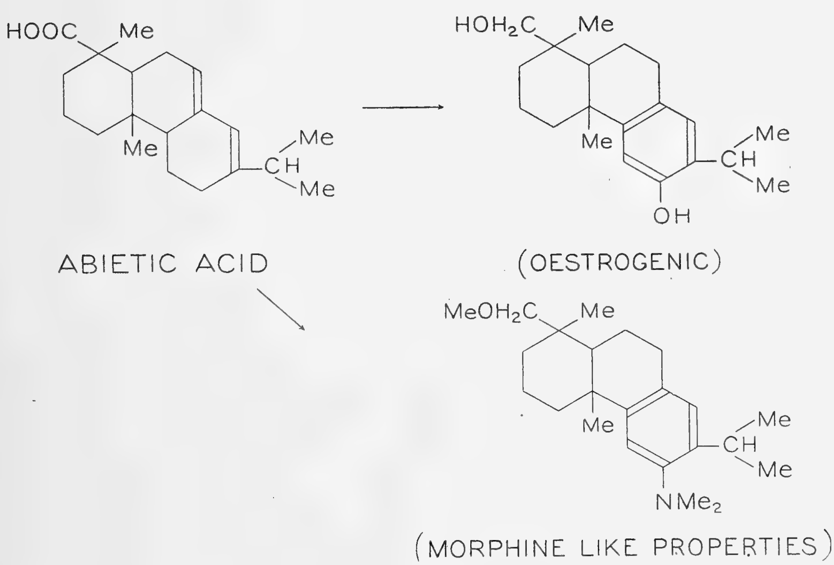
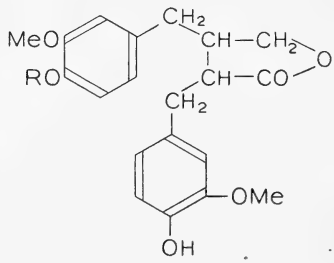


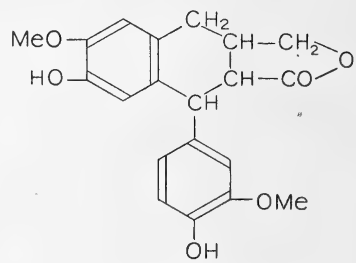
Fig. 11.

abietic acid, one of the cheapest of organic chemicals, into compounds of high physiological activity.

The heart-shakes of *Podocarpus spicatus*, "matai", however, contain two resinols or lignanes of a different type, matairesinol and conidendrin. The former was first isolated by Easterfield and Bee (1910), the latter by Haworth, Richardson and Sheldrick (1935) and Briggs and Peak (1936). Their constitutions have been established by degradation (Haworth and Richardson, 1935; Briggs, Peak and Woolloxall, 1935) and by synthesis by Haworth and co-workers in a brilliant series of investigations in this field. The monomethyl ether of matairesinol occurs as a glucoside in the seeds of the burdock, *Arctium lappa* (Shinoda and Kawagoe, 1929). It may be not without interest that a potent antibiotic has also been isolated from the same source.



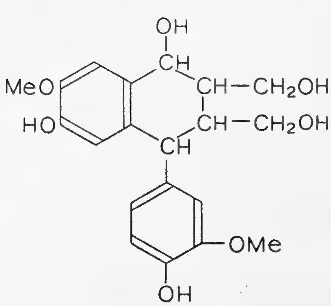
MATAIRESINOL (R=H)
ARCTIGENIN (R=Me)



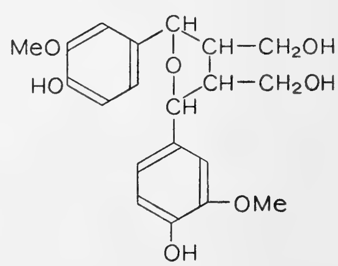
CONIDENDRIN

Fig. 12.

In the heart-shakes of *Olea cunninghamii*, "maire", a lignane of similar type occurs, isoolivil, isomeric with the olivil obtained from the European olive (Briggs and Frieberg, 1937).



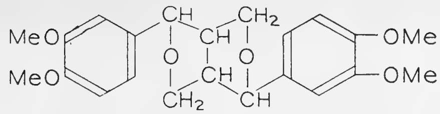
ISOOLIVIL



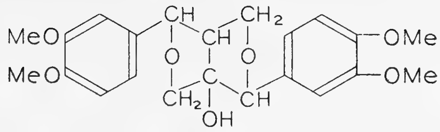
OLIVIL

Fig. 13.

Two representatives of this class have been isolated in Australia, eudesmin from the kinos of *Eucalyptus hemiphloia* (Robinson and Smith, 1915) and gmelinol from the wood of "colonial beech", *Gmelina leichhardtii* (Smith, 1913; Birch and Lions, 1938; Harradence and Lions, 1940). The constitution of eudesmin has been established, while gmelinol is probably its hydroxy derivative.



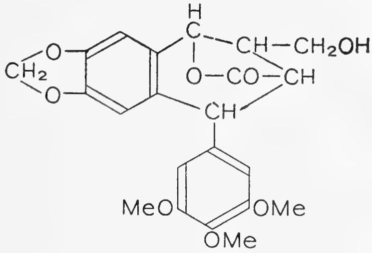
EUDESMIN



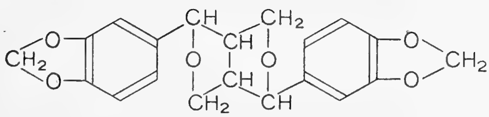
GMELINOL

Fig. 14.

The whole series of lignanes has been reviewed by Haworth (1936, 1942), some of which have interesting properties. Podophyllotoxin has a strong purgative action while α-sesamin and its diastereoisomer, l-asarinin, have a synergistic effect towards pyrethrum extracts as insecticides (Haller, McGovran, Goodhue and Sullivan, 1942).



PODOPHYLLOTOXIN



SESAMIN

Fig. 15.

Matairesinol, isoolivil and their simple derivatives, however, have no such synergistic action.

Alkaloids.

Lycopodiaceæ*.

*Lycopodium species**.

Some of the New Zealand endemic species are under investigation by Manske in extension of his previous work on the alkaloids of this genus (for a summary see Manske, 1944).

GRAMINEÆ*.

Lolium perenne, L. temulentum, L. multiflorum, Festuca arundinacea, Setaria* lutescens.*

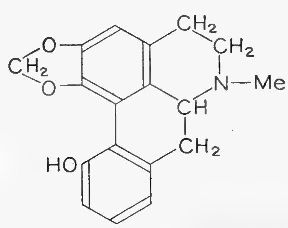
During the autumn of 1939 a serious outbreak of facial eczema occurred in New Zealand. In a search for a probable cause the fodder of the animals was investigated and a series of new alkaloids, the main members being named perloline and perlolidine, were discovered in the above grasses, all introduced species—but only at periods of flush of growth (Grimmett and Melville, 1943 ; Grimmett and Waters, 1943 ; Reifer and Bathurst, 1943 ; Bathurst, Reifer and Clare, 1943 ; Cunningham and Clare, 1943 ; Shorland, White and Grimmett, 1943 ; Shorland, 1943). This is one of the few records of an alkaloid occurring in the large order of Gramineæ. When fed to animals, however, perloline failed to produce facial eczema (for further details see Clare, 1944).

From the investigations by White and Reifer (1945) it would appear that perloline is a harmine derivative, $C_{40}H_{34}O_7N_4$, containing four methoxy groups, an alcoholic group, four tertiary nitrogen atoms only two of which are basic. Oxidation of perloline yields perlolidine, $C_{25}H_{18}O_2N_4$, the other isolated base, both of which are very strongly fluorescent.

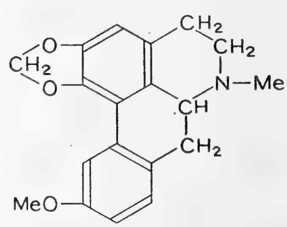
MONIMIACEÆ*.

Laurelia novæ-zealandiæ, " Putakea ".

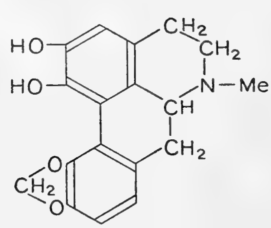
The bark of this tree, which grows abundantly in swampy forests, contains three most important alkaloids, pukateine, laureline and laurepukine. The constitutions of the first two alkaloids, first isolated by Aston (1901, 1909, 1910)



PUKATEINE



LAURELINE



LAUREPUKINE(?)

Fig. 16.

have been elucidated by Barger, Girardet and Schlittler (1931, 1932) and confirmed by synthesis.

The constitution of laurepukine still awaits final confirmation by degradation and synthesis.

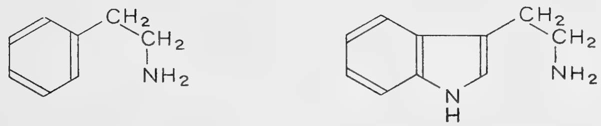
A preliminary report on the pharmacology of pukateine was made by Malcolm (1909) and a detailed examination by Fogg (1935), who found that it possessed strong analgesic properties, similar to morphine but without its after effects.

New South Wales has members of this tribe in the genera *Daphnandra*, *Ætherosperma* and *Doryphora*, from each of which alkaloids have already been isolated. *Daphnandra micrantha*, first investigated by Bancroft (1886), has been shown by Pyman (1914) to contain three alkaloids, daphnandrine, $C_{36}H_{38}O_6N_2$, micranthine, $C_{36}H_{32}O_6N_2$, and daphnoline, $C_{34}H_{34}O_6N_2$, of still unknown structure. On phytochemical grounds it would suggest that they are constituted similarly to the alkaloids of pukatea but with two molecules condensed together through possible ether linkages.

Other New Zealand species of the Monimiaceæ are under investigation.

LEGUMINOSÆ*.

In a comprehensive study on endemic and introduced species of this family White (1946) has examined over 210 species and varieties. It is only necessary here, however, to discuss those endemic to New Zealand or Australia. Of the 14 examined which are endemic to New Zealand all were alkaloid-free, viz. *Carmichaelia australis*, *C. compacta*, *C. flagelliformis*, *C. gracilis*, *C. grandiflora*, *C. odorata*, *C. prona*, *C. subulata*, *C. williamsii*, *Chordospartium stevensoni*, *Clianthus puniceus*, *Corallospartium crassicaule*, *Notospartium carmichaelia*, *N. glabrescens*.



β-PHENYLETHYLAMINE TRYPTAMINE

Fig. 17.

The following species occurring in New South Wales were also found to be alkaloid free: *Goodia lotifolia*, *Daviesia latifolia*, *D. corymbosa*, *Dillwynia cinerascens*, *Jacksonia scoparia*, *Oxylobium ellipticum*, *Swainsona galegifolia*, *Kennedya prostrata*, *K. rubicunda*, *Cassia artemesioides*, *C. sophera*.

Twenty-eight Australian species of Acacia growing in New Zealand were examined, but high concentrations of an alkaloid, identified as β-phenylethylamine, were found only in a section of the genus with uninerval phyllodes and flowers in racemes, viz. *Acacia hakeoides*, *A. linifolia*, *A. linifolia* var. *prominens*, *A. lunata*, *A. pravissima*, *A. suaveolens*, *A. cultriformis*, *A. podalyriæfolia*. The same base with other alkaloidal material was isolated from *A. longifolia* and *A. floribunda*. Other species gave indications by odour of the presence of basic material, viz. *A. acinacea*, *A. baileyana*, *A. decurrens*, *A. decurrens* var. *dealbata*, *A. decurrens* var. *mollis*, *A. drummondii*, *A. elata*, *A. falcata*, *A. leprosa*, *A. linearis*, *A. melanoxylon*. *A. pycnantha*, *A. retinoides*, *A. saligna*, *A. stricta*, *A. verticillata*, *A. vestita*, as well as *Albizzia julibrissin* and *A. lophantha*.

From *Acacia floribunda* and *A. pruinosa* tryptamine was isolated in addition to β-phenylethylamine, which has only previously been found in traces in plants, mainly parasites and fungi, while tryptamine has not previously been found naturally in plants or animals. The occurrence of these bases is of considerable interest in the biogenesis of alkaloids (Robinson, 1936) and in their synthesis under physiological conditions (Hahn and Schales, 1935 ; Schöpf and Bayerle, 1934); however it is remarkable that more complicated alkaloids are absent in these species.

SOPHOREÆ*.

The alkaloids of the seeds of three of the five listed endemic species have been examined in detail.

Sophora microphylla.

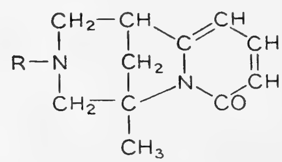
The seeds contain mainly methylcytisine and matrine, a little cytisine and two further new alkaloids in minute amounts (Briggs and Ricketts, 1937).

Sophora tetraptera.

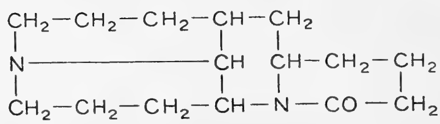
The alkaloids here are mainly matrine, a little methylcystine and one of the new bases from *S. microphylla*, again in minute amount (Briggs and Taylor, 1938).

Sophora chathamica.

This species from the Chatham Islands has been differentiated from *S. microphylla* on the slender evidence of slight changes of the juvenile form. The alkaloids from the seeds are identical with those of *S. microphylla*, which would suggest identity (Briggs and Russell, 1942*a*).



CYTISINE (R=H)
METHYLCYTISINE (R=Me)



MATRINE (?)

Fig. 18.

The new alkaloid occurring in *S. microphylla*, *S. tetraptera* and *S. chathamica* (?) also occurs in much larger quantity in the Hawaiian species, *S. chrysophylla*, and has been named sophochrysine (Briggs and Russell, 1942*b*).

The constitutions of cytisine and methylcytisine have already been elucidated, a provisional structure of matrine has been suggested (Henry, 1942), but the empirical formula of sophochrysine is still uncertain.

Recently an investigation has been made (Briggs and Mangan, 1946) on the seeds of an undescribed but possibly new species growing at Anawhata, near Auckland. The major alkaloid has been identified as methylcytisine with some cytisine. The presence of only a very small amount of matrine indicates a sharp difference from those endemic species already examined and would thus support the establishment of a new species.

CORYNOCARPACEÆ.

Corynocarpus lævigata, "Karaka".

The kernels of the berries of this coastal tree were cooked and thus used by the Maoris for food. The raw material, however, contains a poisonous glucoside, karakin, $C_{20}H_{30}O_{19}N_4$, which is destroyed in the cooking process. It was first isolated by Skey (1871) and later investigated by Aston and Easterfield (1901, 1903), Carrie (1934) and Carter (1943).

On hydrolysis different products are obtained with various reagents. According to Carter the initial hydrolysis proceeds according to the following equation :

$$\underset{\text{Karakin}}{C_{20}H_{30}O_{19}N_4} + 3H_2O \rightarrow \underset{\text{Hiptagenic acid.}}{2C_3H_5O_4N} + \underset{\text{Sugar derivative}}{2C_7H_{13}O_7N}$$

forming hiptagenic acid and a sugar derivative. The former compound is also obtained as a hydrolytic product of hiptagin, a similar glucoside from the bark of the tree, *Hiptage madablota* (Gorter, 1920). The sugar derivative loses carbon dioxide on boiling to form an aminohexose, hydrolysed further with alkali to a hexose, from which glucosazone was isolated.

Hiptagenic acid according to Gorter has the constitution

$$\begin{array}{l} HO{-}NH{-}\underset{\|}{C}{-}\underset{|}{C}{=}CHOH \\ \phantom{HO{-}NH{-}}OOH \end{array}$$

while Carter regards it as

$$HO{-}N{=}CH{-}CH(OH){-}COOH.$$

The final solution of the constitution of these unique compounds still awaits further experiment.

SOLANACEÆ*.

*Solanum aviculare**.

The fruit of this shrub, which occurs both in New Zealand and New South Wales, was first investigated by Levi (1930), who isolated a glycosidic alkaloid, thought to be new but identified later by Bell and Briggs (1942) as solasonine occurring in *S. sodomæum* and *S. xanthocarpum**. Based on degradative studies by Oddo and co-workers, Rockelmeyer and Briggs, Newbold and Stace (1942 ; see this paper for references) the following formula was suggested by Briggs *et al.* (1942).

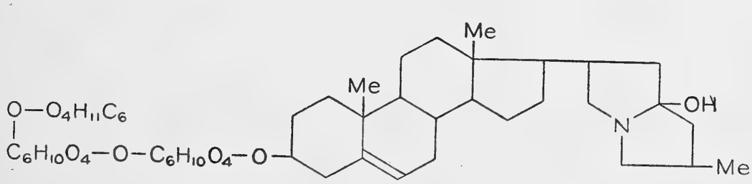
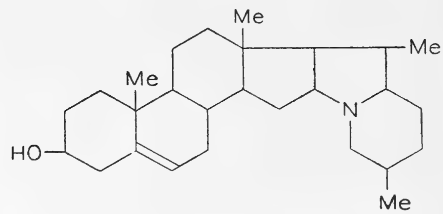


Fig. 19.

It differs only as the carbinol amine of solanine, from *S. tuberosum*, for which a similar structure had been proposed. It contains the cholesterol carbon skeleton and it was assumed that the basic portion was joined to the ring structure by only one point of attachment from the isolation of Diels' hydrocarbon on selenium dehydrogenation. Recently, however, Prelog and Szpilfogel (1942) have identified, through synthesis, the basic dehydrogenation product of

solanidine as 2-ethyl-5-methylpyridine, and to accommodate this fact they proposed a modified structure for solanidine.

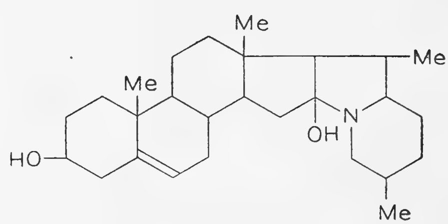


SOLANIDINE

Fig. 20.

A comparison of the rotations of solanidine and its derivatives with those of similar derivatives of cholesterol (Prelog and Szpilfogel, 1944) has shown that the two compounds are directly related stereochemically, and this constitution of solanidine has now been confirmed by Uhle and Jacobs (1945) through the partial synthesis of dihydrosolanidine from sarsasapogenin of known constitution.

Dehydrogenation of solasodine gives a basic portion whose picrate has the same melting point as that of 2-ethyl-5-methylpyridine (Rochelmeyer, 1937) indicating their identity. Solasodine, therefore, probably has the same skeleton as solanidine, but the hydroxyl group has now been attached to C_{16}, thus obviating the formation of a nine-membered ring for the *chano* compounds on the previous formulation.



SOLASODINE

Fig. 21.

Experiments on the interconversion of solanidine and solasodine are in progress.

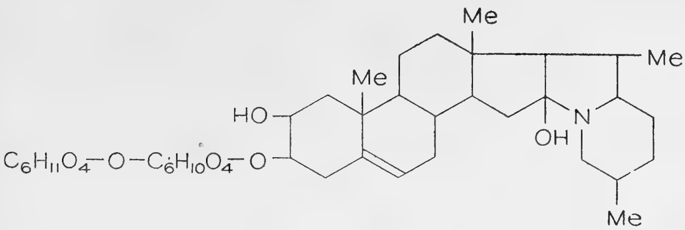
Solanum auriculatum.

The alkaloid of the fruit of this introduced species, now naturalised in various parts of New Zealand, was first considered to be identical with solasonine (Anderson and Briggs, 1937) but later shown to be a new alkaloid, solauricine, but extremely closely related to solasonine (Bell, Briggs and Carroll, 1942; Briggs and Carroll, 1942).

Solanum marginatum.

From the fruit of this introduced species, but now naturalised in the Marlborough Sounds, a new alkaloid, solmargine, has been isolated. Experiments

to date in the author's laboratory (Briggs, Harvey and Odell, 1946) have shown it to be a rhamno-glucoside of the following probable constitution :



SOLMARGINE

Fig. 22.

The structure of the veratrine alkaloids, obtained from a genus far removed from the Solanaceæ and whose relationship to the *Solanum* alkaloids was suspected, has now been proved experimentally by the formation of 1 : 2-cyclopentenophenanthrene (but no Diels' hydrocarbon) and 2-ethyl-5-methylpyridine on selenium dehydrogenation of rubijervine (Jacobs and Craig, 1945).

Over two dozen species of *Solanum* in New South Wales are open to investigation, while the pharmacology of these alkaloids has yet only been poorly investigated. Since they are steroid alkaloids, specific tests characteristic of the other various types of steroids should be carried out.

COMPOSITÆ*.

Senecio kirkii.*

Of the 30 species found in New Zealand one, *S. lautus*, extends to Australia, while the rest are all endemic.

Manske (1944) has recently surveyed the alkaloids from this genus, the largest genus of the Compositæ, if not of flowering plants generally, containing probably at least 1,000 species. It would appear that each species elaborates a different alkaloid or a different series of alkaloids and Manske has shown that species can be differentiated by their alkaloidal content where there is practically no difference in their morphological characters. The pioneering work of Baker and Smith correlating the chemistry of the essential oils and the morphological characters of the genus *Eucalyptus* thus has its analogies in the alkaloid field.

Work has now been commenced on the alkaloids of the New Zealand species and from *S. kirkii* a new crystalline base senkirkine, $C_{18}H_{25}O_6N$, m.p. 197–198° (picrate, m.p. 226–226·5°) has been obtained (Briggs, Mangan and Russell, 1946).

Eighteen species are listed for New South Wales, none of which has yet been examined chemically.

Brachyglottis repanda.

This shrub or small tree belongs to a genus of two or possibly even one closely allied to Senecio and endemic to New Zealand. The plant is poisonous to stock causing " staggers ". The leaves definitely contain an alkaloid in small yield, possibly allied to the Senecio alkaloids but it has not yet been fully investigated.

COLOURING MATTERS.

TAXACEÆ*.

*Podocarpus** *spicatus*, " Matai ".

In working up the mother liquors of matairesinol and conidendrin, three colouring matters have been isolated, the flavonol, quercetin, and two new coloured compounds A and B of still unknown structure.

The absorption spectrum of A, which is isomeric but not identical with rhamnazin, does not correspond to that of a flavonol (Briggs, 1946).

VERBENACEÆ*.

*Vitex** *littoralis*, " Puriri ".

Two colouring matters were isolated from the wood of this tree by Perkin (1898), which, after hydrolysis, yielded the aglycones vitexin and homovitexin. Vitexin has also been isolated as its glucoside by Barger (1906) from *Saponaria officinalis*. Degradative work by Perkin (1900), Barger and Péteri (1939) has directly related it to apigenin of known structure and alternative formulæ have been proposed.

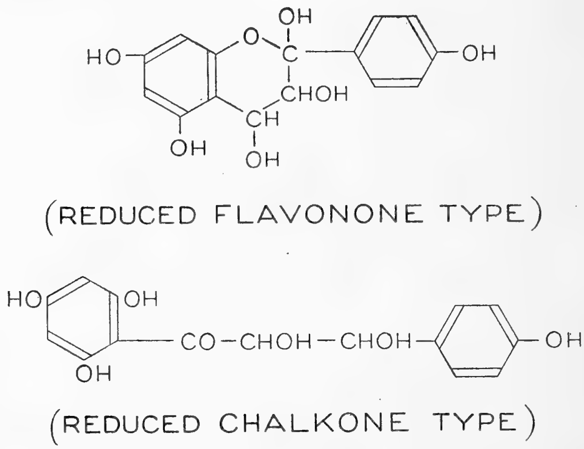


Fig. 23.

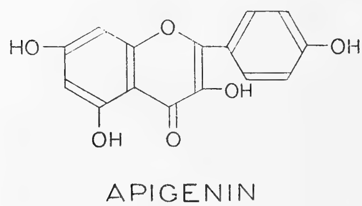


Fig. 24.

The absorption spectrum of vitexin should throw considerable light on its constitution.

RUBIACEÆ*.

This family is one of the largest and best defined families in the plant kingdom, containing more than 450 genera and 5,500 species.

Coprosma Species.*

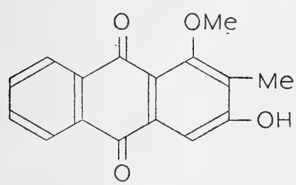
The inner bark of numerous species was extensively used by the Maoris for colouring their flax fibre (Te Rangihiroa, 1911). During the Great War of 1914–1918, when synthetic khaki dyes were difficult to obtain, Aston (1917, 1918*b*, *c*, 1919*b*, 1923*a*) investigated species of this genus for dyestuffs and showed that a number were suitable for the purpose. From *C. australis* he isolated two pigments which were not, however, identified nor characterised.

He has also shown that differences are exhibited by many species in the colour of the bark and that given on addition of sodium hydroxide solution, whence it would appear that a diversity of coloured compounds is present in this genus.

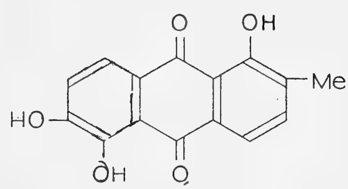
This work has now been continued and a series of anthraquinone colouring matters has been obtained (Briggs, Craw, Dacre, Nicholls and Ronaldson, 1946).

C. australis.

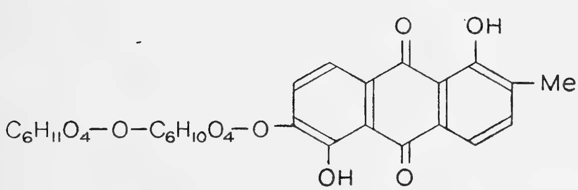
The two compounds isolated by Aston have been identified as rubiadin methyl ether and morindone. In addition two more compounds have been obtained by chromatographic adsorption, morindin, the rhamno-glucoside of morindone, and another, yet unidentified. As morindone is a powerful dyestuff giving a wide variety of colours with different mordants and the colouring matters are present to the phenomenal extent of 24% of the dry weight of the bark of this tree, it should form a valuable raw material for the home-dyer.



RUBIADIN METHYL ETHER



MORINDONE

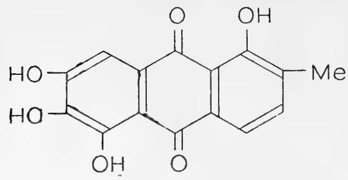


MORINDIN

Fig. 25.

C. areolata.

By chromatographic adsorption two colouring matters have been isolated, rubiadin methyl ether and a new pigment, areolatin, for which the following provisional formula is proposed.



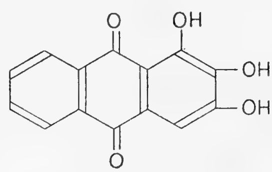
AREOLATIN

Fig. 26.

Areolatin is also an excellent dyestuff and again the yield of colouring matters from the bark is phenomenally high (18% of the dry weight).

C. lucida.

Eight colouring matters have been isolated, apparently different from those already isolated, of which one has been identified as anthragallol, the first record of its occurrence in nature.



ANTHRAGALLOL

Fig. 27.

C. rubra.

Chromatographic adsorption indicates the presence of three coloured compounds, one of which has been identified as rubiadin methyl ether.

The glycoside asperuloside, first isolated from *Asperula odorata* and also from the leaves of *C. lucida, C. robusta* and *C. repens* (Hérissey, 1933). is widely distributed in the bark as well and has now been identified in that of *C. lucida, C. robusta, C. repens* and *C. arborea.* Asperuloside, $C_{18}H_{22}O_{11},H_2O$, which is colourless, on hydrolysis yields a greenish-black insoluble compound, possibly an hydroxylated naphthaquinone derivative.

It is hoped to make a comprehensive survey of these colouring matters not only from their intrinsic chemical interest but also from a systemic point of view in the elucidation of the problem of hybridisation which occurs commonly among species of this genus (Allan, 1930).

Tannins.

A number of other trees, shrubs and plants were also used by the Maoris for dyeing. Usually the fibres were soaked in extracts of the bark containing tannin and then in ferruginous springs so that a black colour, in reality an ink, was produced. Some of these have been examined for tannin content, and although high in some cases they do not compete with normal sources from Acacia species. Quantities of the bark of *Phyllocladus trichomanoides* were formerly exported for

tanning purposes, mostly to France for glove leather. The following list is given by Aston:

	%
Phyllocladus trichomanoides	29
P. glauca	29
Weinmannia racemosa	19–23
W. sylicola	10–13
Nothofagus fusca	9–16
N. solandri	13
Metrosideros lucida	9
M. robusta	11
Elæocarpus dentata	6–10
E. hookerianus	4–10
Dacrydium cupressinum	10
Podocarpus ferrugineus	7
Fuchsia excorticata	3–4
Eugenia maire	17
Coriaria ruscifolia	2–16

In addition Aston points out that the following species of lichens grow in New Zealand which are used commercially for dyeing in Scotland and Ireland in the preparation of Harris, Lewis, Donegal and Shetland homespun materials, viz. *Parmelia caperata*, *P. saxatelis*, *P. parietina*, *P. perlata*, *P. conspersa*, *Lecanora tartarea*, *Cetraria islandica*, *Gyrophora cylindrica*, *Ochrolechia parella* and *Teloschistes flavicans*.

Saponins.

Owing to the relative ease with which sarsasapogenin may be transformed into the sex hormones which are only available in minute amounts from other natural sources such as urine, a search has been made for further sources of steroid saponins. In what is probably the most extensive report yet made on natural products Marker, Wagner, Ulshafer, Wittbecker, Goldsmith and Ruof (1943) have described a summary of their investigations of over 300 species, from which known saponins were isolated in addition to 14 new ones whose structures were elucidated. Many of the species belonged to the Agavaceæ, which in New Zealand is represented by the familiar cabbage tree, *Cordyline australis*, three other species of the same genus and the common flax, *Phormium tenax*. The roots of these plants are therefore worthy of investigation for the same purpose.

During investigations on the saponins of *Pomaderris elliptica*, "Gum Diggers' Soap", and two introduced species, *Zantedeschia æthiopica*, "arum lily", and *Arum maculatum*, which are still incomplete, a survey of the literature revealed a phytochemical fact apparently not generally recognised. Two main types of saponins exist, one of steroid and the other of triterpenoid acid structure. From those whose structure has been investigated in some detail it would appear that the steroid type occur only in the monocotyledon class of the Angiospermæ, while the triterpenoid type are restricted to the dicotyledons.

A saponin, perhaps identical with the glycoside pittosporin, occurs in the leaves of *Pittosporum corrifolium*, *P. crassifolium*, *P. eugenioides* and *P. huttonianum*. The same compound has also been found to occur in species whose habitat lies outside New Zealand (Klein, 1933, p. 1135).

Fibres.

Phormium tenax, "Flax".

Besides its possible use as a source of saponins the New Zealand flax is one of our most important plants from another economic point of view. The fibre is of very high quality, and although production fluctuates, up to 1939 over 180,000 tons, to the value of nearly £10,000,000, have been exported.

Analyses have been made by various workers (Hutton, 1869 ; Church, 1873 ; Aitken, 1928 ; McIlroy, 1944), while a preliminary study has been made on the hemicellulose portion by McIlroy, Holmes and Mauger (1945). From this it would appear that the hemicellulose is constituted of a main chain containing nine or ten xylo-pyranose residues united by 1 : 4-β-linkages, terminated at the reducing end by a complex, highly branched acid nucleus containing d-glucuronic acid as one component.

Sea-weeds.

Some of the New Zealand species have been investigated for their iodine, potassium and other mineral content. During the recent war, when supplies of agar-agar were cut off from Japan, a search was made in New Zealand for species suitable for the purpose. Due to the efforts of Miss Moore, two species, *Pterocladia lucida* and *P. capillacea*, were found suitable and collections were arranged over the coastal areas of the North Island. In three years nearly 250 tons were collected and processed. The agar-agar obtained is of excellent quality and has approximately twice the gelation strength of the Japanese product (Moore, 1944, 1946).

As yet no attempt has been made to exploit New Zealand sea-weeds for the manufacture of sea-weed rayon, the fundamental constituent of which is alginic acid (Speakman, 1945). A recent survey of *Macrocystis* shows that the Cook Strait area alone could provide an annual harvest of about 4,000 tons of dry kelp at an estimated cost of £10 per ton (Melville, 1946).

Antibiotics.

Although the first examples of antibiotics were discovered in the lower plant forms, there are now numerous references to their occurrence in the higher forms. With its wealth of endemic species New Zealand offers wide scope for further investigation along these lines.

In conclusion, for my part of the work carried out on the plant products of New Zealand I should like to express my sincere thanks to a willing band of co-workers who, over the years, have helped to elucidate some of Nature's secrets and have found joy in doing so. I am also greatly indebted to the Royal Society of New Zealand, the Chemical Society, London, the Australian and New Zealand Association for the Advancement of Science, the Research Council of the Department of Scientific and Industrial Research, New Zealand, for research grants, and Imperial Chemical Industries for gifts of chemicals.

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STUDIES ON COLOUR REACTIONS FOR SUGARS.

PART II. THE ISOLATION OF THE PRECURSOR AND OF THE BLUE COMPOUND OBTAINED BY THE INTERACTION OF THYMOL, HYDROCHLORIC ACID AND FERRIC CHLORIDE WITH GLUCOSE.

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Recently a simple colour reaction of monosaccharides with a reagent consisting of thymol, ferric chloride and hydrochloric acid was described (Bolliger, 1943) which subsequently was also found to be a useful test for the detection of small amounts of thymol.[2] The present paper is the result of an endeavour to isolate and examine the substance or substances responsible for the blue colour obtained with aldoses.

Using glucose, it was possible to isolate two crystalline substances in a pure state from the reaction mixture. One of these, Compound (I) $C_{40}H_{44}O_5$ (m.pt. 283° C.) was yellow and was found to be the precursor of the substance responsible for the blue colour in the original test. The other substance, which was colourless (m.pt. 285–6° C.), was disregarded for the time being as it appeared to play little part, if any, in the colour reaction and was present in relatively small amounts.

On the addition of mineral acids or some of their salts with heavy metals to a solution of (I) dark red colours were obtained. A compound was isolated using hydrochloric acid. This dark red substance, compound (I*a*) was converted back to (I) by removal of hydrochloric acid. Treatment of (I) or (I*a*) with mild oxidising agents such as ferric chloride or dilute hydrogen peroxide produced a red compound (II) which turned blue (II*a*) on the addition of hydrochloric acid and became red again by removal of hydrochloric acid with water. The red (II) and the blue (II*a*) forms were isolated. Compound (II) has oxidising properties and could be reconverted to (I) with reducing agents. (II*a*) has the same properties as the blue compound obtained directly in the colour reaction of glucose with thymol, hydrochloric acid and ferric chloride. The two substances are therefore assumed to be identical.

The figures obtained for (I) by analyses and molecular weight determinations suggest a compound $C_{40}H_{44}O_5$. This is further supported by the analytical figures obtained from derivatives. The red compound (I*a*) seems to be a hydrochloride hydrate of (I) which dissociates in acetone, the medium used for molecular weight determination.

The analytical figures obtained for Compound (II), $C_{80}H_{86}O_9$, suggest a doubling of the molecule of compound (I) and simultaneous loss of hydrogen and oxygen. The blue form (II*a*) is apparently a hydrochloride hydrate of the red form as indicated by behaviour and analysis.

[1] Working under a grant from the National Health and Medical Research Council.

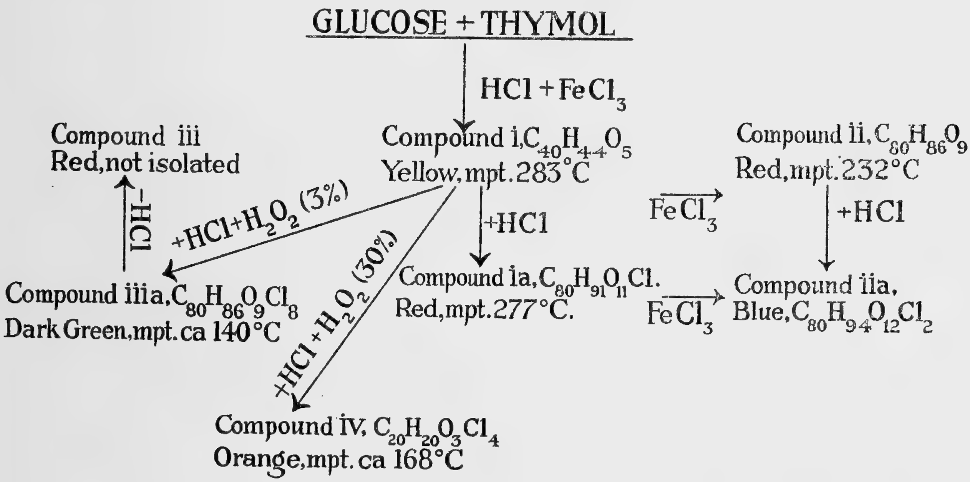
[2] In a patient suffering from cerebral torulosis and treated with thymol, the presence of thymol in the cerebro-spinal fluid could be demonstrated by means of this colour test some hours after the intraventricular but not after oral administration.

The deep green compound (III*a*), $C_{80}H_{86}O_9Cl_8$, was obtained by a simultaneous oxidation and chlorination of (I). On washing with water it loses hydrochloric acid and changes into a red form (III), which has not been isolated. From this and from analytical figures one or two of the chlorine atoms must be present as one or two molecules of hydrochloric acid.

A remarkable parallelism exists in the behaviour of the compounds (I), (II) and (III). On the addition of mineral acids in high concentration to their solutions they change to deeper coloured substances, i.e. from yellow to red in the case of (I), from red to brilliant blue in the case of (II), and from red to deep green in the case of (III). In all these instances the original colour could be restored by diluting the acid.

Simultaneous strong oxidation and chlorination with 30 % hydrogen peroxide and hydrochloric acid gas resulted in a compound (IV) with a chlorine content of about 32 % ($C_{20}H_{20}O_3Cl_4$). In contrast to the previously mentioned oxidation products of this series it is characterised by a yellow-orange colour and no hydrochloric acid could be washed out with water.

The following diagram summarises these reactions and gives the colour of the compounds in chloroform.



Acetylation of (I) with acetyl chloride and pyridine gave a compound (V) $(C_{44}H_{48}O_7)_2$ indicating that two acetyl groups had entered the molecule which apparently united with a similar molecule in this process.

Acetylation with acetic anhydride resulted in a product (Compound VI) ($C_{44}H_{50}O_8$) which is monomolecular and which contains more oxygen than (V). Benzoylation using benzoyl chloride and pyridine yielded a compound (VII) whose analytical figures $(C_{54}H_{52}O_7)_2$ indicated that two benzoyl groups have entered the molecule of (I) and that the compound formed is also bimolecular. Acetylation and benzoylation abolish the property of (I) to form deeply red coloured molecular compounds with acids and their salts and further, to undergo changes to red or deep blue in the presence of ferric chloride.

Experimental.

Preparation of (I).

Ferric chloride (150 gms.) and glucose (40 gms.) in water (80 ml.) and thymol (98 gms.) in alcohol (300 ml.) were mixed and heated with hydrochloric acid (2·5 l.) on a water bath till the solution darkened considerably. Then the temperature was maintained at approximately 85° C. for about 8 hours. A dark purple red oil formed which floated on the surface of the reaction

mixture. After standing overnight 5 to 10 volumes of water were added and the supernatant oil which by then had become partially solid and had also progressively darkened, was removed. This was boiled in several litres of water till the thymol had disappeared and the reaction mixture, which by then was a black solid mass, was dried and then heated with anisol (200 ml.). After standing for several hours the dark insoluble solid was filtered off and ground in a mortar with cold benzene. The remaining green powder was dissolved in a mixture of ethyl acetate and benzene 1 : 4. After filtering, the solution was chromatographed on aluminium oxide. A number of distinctive bands formed, the lowest coloured one being bright yellow, those higher up being of bluish, or reddish colour. From the colourless filtrate a small amount of colourless crystals was isolated.

The bright yellow band deposited on the column was eluted with the ethyl acetate-benzene mixture. This eluate was passed through a second column of alumina. The final eluate was a strongly green fluorescent, yellow solution. It was evaporated to near dryness, and after the addition of benzene the yellow precipitate was filtered off and washed several times with benzene and then recrystallised from anisole. The compound thus obtained was called compound (I). The bluish and reddish bands were subsequently eluated with the ethylacetate benzene mixture and were found to contain considerable amounts of an oxidised form of compound (I). The remaining darkish pigment which was more difficult to eluate was discarded.

Properties of (I).

After repeated chromatography followed by recrystallisation from anisole (I) was found to consist of canary yellow rods which melt at 283° C. (I) is readily soluble in alcohol, acetone, ethyl acetate, glacial acetic acid, and ether ; and sparingly soluble in chloroform, carbon tetrachloride ; and insoluble in petrol ether, benzene and water. It is also insoluble in sodium bicarbonate and sodium carbonate solution. It is soluble in sodium hydroxide, yielding a blue coloured solution from which almost immediately a deep blue compound begins to precipitate. On the addition of concentrated hydrochloric, sulphuric, perchloric or phosphoric acids, the yellow solutions of (I) change to a deep red. These solutions when poured into water give red precipitates ; that obtained with hydrochloric acid will be described in detail (compound I*a*). A similar change of colour also takes place on the addition of solutions of heavy metal salts such as stannous chloride, silver nitrate, etc., in organic solvents. With silver nitrate the red colour within a few hours changes to a brilliant blue, while metallic silver is precipitated, thus indicating the reducing properties of (I) which at the same time is converted into a blue compound (II*a*). Other oxidising agents such as ferric chloride or hydrogen peroxide in strong acid solution also produce a brilliant blue after shaking the mixture for some time or heating it. It was also observed that solutions of (I) in chloroform exposed to air for several days turned blue. On the addition of zinc dust to the blue acid reaction mixture, the blue colour disappears and the solution reverts to its original yellow tint and its green fluorescence. A blue solution is also obtained on warming (I) with sodium hydroxide for a few minutes and immediately acidifying it with concentrated hydrochloric acid. (I) does not give a dinitrophenylhydrazone.

With benzene (I) readily forms an addition compound which has been isolated and analysed.

$C_{40}H_{44}O_5$ Cal : C, 79·47 ; H, 7·38 ; mol. weight, 604.

Found : C, 79·63 ; H, 7·49 ; mol. weight, 565,595.

Benzene addition product of (I).

$C_{40}H_{44}O_5+C_6H_6$ Cal : C, 80·70 ; H, 7·37 ; benzene 10·2%.

Found : C, 80·83 ; H, 7·54 ; benzene 10·4% (heating at 150° C.).

Compound (Ia).

0·1 gm. of (I) was dissolved in absolute alcohol (5 ml.) and hydrogen chloride was bubbled into the yellow solution till it became saturated. The solution turned a deep red and after an additional fifteen minutes the deep red alcoholic solution was poured into water. The red precipitate (I*a*) was filtered and washed with large amounts of water. After drying in the desiccator over sodium hydroxide (I*a*) became a maroon powder which was found to melt at 277° C. Yield, 0·1 gm. (I*a*), however, showed evidence of decomposition at about 140–150° C., when its colour changed from red to green.

Compound (I*a*) dissolves in cold alcohol with brilliant red colour which turns yellow on heating. The cold solutions of (I*a*) are yellow in benzene, acetone, ethylacetate and chloroform. The chloroform solution, however, readily turns blue on standing for several hours. (I*a*) is not soluble in sodium carbonate, but dissolves in sodium hydroxide, yielding a blue solution from which a blue precipitate rapidly forms. The result of mild oxidation of (I*a*) is the same as that of (I) and a blue compound (II*a*) is readily obtained. Even if (I*a*) in solid form is left exposed to air for several days it develops a blue tint. Red solutions of (I*a*) chloroform, ethyl acetate, etc., containing hydrogen chloride, turned yellow as soon as the acid is washed out or extracted with water. The resulting crystalloid after precipitation with petroleum ether is the original compound (I).

$(C_{40}H_{44}O_5)_2HCl.H_2O$. Cal.: C, 76·0; H, 7·26; Cl, 2·81; mol. weight, 1,263.
Found: C, 75·25; H, 7·45; Cl, 3·08; mol. weight, 670.

Compound (II).

The oxidation product of (I). To 2 grammes of compound (I) in ethyl acetate (100 ml.) was added solid ferric chloride (4 gms.). On standing the solution turned green and ultimately blue. After washing with water the now dark red solution was chromatographed and the red filtrate concentrated. On standing, deep purple crystals appeared which were recrystallised from ethyl acetate. Compound (II) melts with decomposition at 232° C.

On adding concentrated hydrochloric acid to the red solution of (II) the colour immediately changed to a brilliant hue. The red colour could be restored by washing the acid from the solution. The blue colour present in acid solutions of (II) was removed by the addition of zinc dust and (II) was reduced to the yellow compound (I).

$C_{80}H_{86}O_9$. Cal.: C, 80·64; H, 7·28; mol. weight, 1,191.
Found: C, 80·79; H, 7·30; mol. weight, 980.

Compound (IIa).

The red compound (II) was taken up in chloroform. On the addition of a saturated alcoholic solution of hydrogen chloride a dark green tarry precipitate formed on the walls of the vessel. After pouring off the chloroform the remaining dark green semi-solid was dissolved in absolute alcohol. The colour of the solution was a dark green which turned a deep blue on the addition of a few drops of water. The alcoholic solution when evaporated *in vacuo* over sodium hydroxide yielded a dark blue residue (compound II*a*).

$C_{80}H_{86}O_9.2HCl.3H_2O$. Cal.: C, 72·88; H, 7·21; Cl, 5·38.
Found: C, 72·61; H, 7·41; Cl, 5·06.

Compound (IIIa).

Oxidation and simultaneous chlorination of (I). 0·1 gm. of (I) was dissolved in alcohol (6 mls.). This solution was saturated with hydrogen chloride as described previously (compound I*a*). Then a solution of hydrogen peroxide (3%) was slowly added drop by drop over a period of several hours. After adding about 1 ml. the colour of the solution turned a deep green-blue. It was then placed in a desiccator containing sodium hydroxide which was evacuated. Within two days standing in the desiccator sufficient of the solvent had evaporated to bring out a bulky, almost black crystalline precipitate which was filtered off, washed with a large volume of water and analysed (compound III*a*). It melted unsharply around 140° C.

(III*a*) was found to be soluble in the usual organic solvents with a green colour. Solutions of (III*a*) in chloroform or similar solvents when washed with water turned a brick red (compound III) and the wash water was found to contain hydrochloric acid. On acidifying this red solution the green colour was restored.

$C_{80}H_{86}O_9Cl_8$. Cal.: C, 64·70; H, 5·83; Cl, 19·08.
Found: C, 64·47; H, 6·08; Cl, 18·6.

Compound (IV).

Energetic oxidation and simultaneous chlorination of (I). 0·4 gm. of (I) was dissolved in alcohol (10 ml.). This solution was saturated with hydrogen chloride. Then hydrogen peroxide

30% was added slowly drop by drop over a period of several hours. After a few drops the red colour of the solution disappeared and changed to yellow, and a yellow precipitate appeared after the addition of about 1 ml. of hydrogen peroxide. After an additional 2 ml. of hydrogen peroxide and a few drops of water, the precipitate (compound IV) was isolated and recrystallised from alcohol and then from petrol ether. Crude yield, 0·6 gm. Compound (IV) consists of orange needles which melt unsharply at 168° C. They possess strong oxidising properties and are readily soluble in practically all organic solvents.

$C_{20}H_{20}O_3Cl_4$. Cal.: C, 53·33; H, 4·44; Cl, 31·5; mol. weight, 450.
Found: C, 52·77; H, 4·45; Cl, 31·4; mol. weight, 514.

Acetylation of (I).

A solution of (I) (0·5 g.) in pyridine (5 mls.) was cooled in ice water and acetyl chloride (2·5 ml.) was added drop by drop. After standing at room temperature for about two hours water was added and the mixture acidified with dilute hydrochloric acid and allowed to stand overnight. The yellow precipitate (compound V) was filtered, washed, dried and recrystallised three times from aqueous alcohol, m.p. 163°.

$(C_{44}H_{48}O_7)_2$. Cal.: C, 76·74; H, 7·04; mol. weight, 1,376.
Found: C, 76·60; H, 7·40; mol. weight, 1,180.

Treatment of (I) with acetic anhydride readily yielded a yellow crystalline material (compound VI, m.p. 165° C.) which analysed as follows:

$C_{44}H_{50}O_8$. Cal.: C, 74·79; H, 7·08; mol. weight, 706.
Found: C, 74·79; H, 7·06; mol. weight, 740.

Benzoylation of (I).

0·5 gm. of (I) was dissolved in freshly distilled pyridine (5 ml.) and the solution was cooled in ice water. Benzoyl chloride (2·5 ml.) was added and the mixture was boiled under reflux for 30 minutes. Then it was cooled and poured into dilute hydrochloric acid. A yellow oil separated out which was extracted with ether. The combined ethereal solutions were washed with dilute hydrochloric acid, sodium bicarbonate and water. After drying over anhydrous sodium sulphate, the ether was distilled off. The residue was an oil which partially crytsallised on cooling. On taking up the residue with alcohol and boiling it with aluminium oxide, it became possible to obtain the greater part of the material in crystalline form (compound VII). After several recrystallisations, pale yellow needles were obtained which melted at 181–182° C.

$(C_{54}H_{52}O_7)_2$. Cal.: C, 79·80; H, 6·44; mol. weight, 1,622.
Found: C, 79·80; H, 6·20; mol. weight, 1,470.

Acknowledgment.

The authors wish to thank Miss J. Fildes, B.Sc., who carried out most of the analyses recorded and Mr. Neil J. Hinks who rendered valuable technical assistance.

Reference.

Bolliger, A., 1943. This Journal, 77, 109.

THE CHEMISTRY OF OSMIUM.

PART I. THE REDOX POTENTIAL OF A TRIVALENT-QUADRIVALENT OSMIUM COUPLE IN HYDROBROMIC ACID.

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A study of the chemistry of osmium recently commenced in this laboratory reveals that only scanty data are available for the energies of the element in the various oxidation states. In the present paper the redox potential of the trivalent-quadrivalent osmium couple has been determined as the first of a projected series of determinations of the potentials of the various oxidation states. Although precise quantitative data of the trivalent-quadrivalent couple were lacking, some idea of the potential could be gathered from potentiometric titrations of osmium compounds, which have been described from time to time. Crowell and Kirschmann (1929), during the potentiometric titration of osmium tetroxide with titanous chloride, observed two inflexions in the curve, the second of which was ascribed to the reduction of Os^{IV} to Os^{III}. Calculation from their results indicates a redox potential of approximately $0 \cdot 3$ volt at 80° C. More recently, Crowell and Baumbach (1935) determined Os^{IV} in solution by reduction with chromous sulphate and calculations based on the potential drop at the end point give a value of $-0 \cdot 15$ volt.

Potentiometric titrations with titanous chloride carried out by the present authors at room temperature gave a value of the redox potential as $0 \cdot 25$ volt. From these approximate determinations, which are always too low to the extent of $0 \cdot 2$ to $0 \cdot 3$ volt, due to failure to reach a true equilibrium, it appeared that the true value lay between $0 \cdot 4$ and $0 \cdot 5$ volt. The value predicted by Latimer (1938), $0 \cdot 85$ volt, appeared to be too high.

The halides OsX_4 and R_2OsX_6 are well known, and OsX_3 and R_3OsX_6 have been claimed to exist, although efforts to isolate either OsX_3 or R_3OsX_6 have not been successful (Claus and Jacoby, 1863 ; Crowell, Brinton and Evenson, 1938). Since osmium exhibits valencies as high as eight, one would expect the instability constants of the quadrivalent and trivalent halide complexes to be appreciable, the latter being the larger. This is confirmed by the isolation of the simple compounds Os_2S_3, Os_2O_3, OsO_2 and OsS_2 from solutions of the complex halides by addition of caustic soda or hydrogen sulphide. By analogy with ruthenium it is also likely that the chemistry of quadrivalent osmium is complicated by hydrolysis at relatively high acid concentrations.

For these reasons it is not possible to measure the true redox potential (at infinite dilution) of the system $OsX_6^{IV} \rightarrow OsX_6^{III} + e$. Therefore the method of measurement consisted of mixing equimolar solutions of potassium hexabromosmate and hexabromosmite in various concentrations of hydrobromic acid, and determining the potential of an inert electrode in a carbon dioxide atmosphere free from oxygen.

The various values are shown in Table 1 and Fig. 1. It was found that the potential fell rapidly with increasing acid concentration, and then much more

TABLE 1.

Potentials of Equimolar Mixtures of Tri- and Quadrivalent Osmium (each 0·00033 Molar) in Hydrobromic Acid at 25° C.

Hydrobromic Acid Concentration. (Normality.)	Potential. (Volts.)
0·11	0·444
1·01	0·392
1·56	0·360
2·81	0·307
3·53	0·290
4·75	0·269

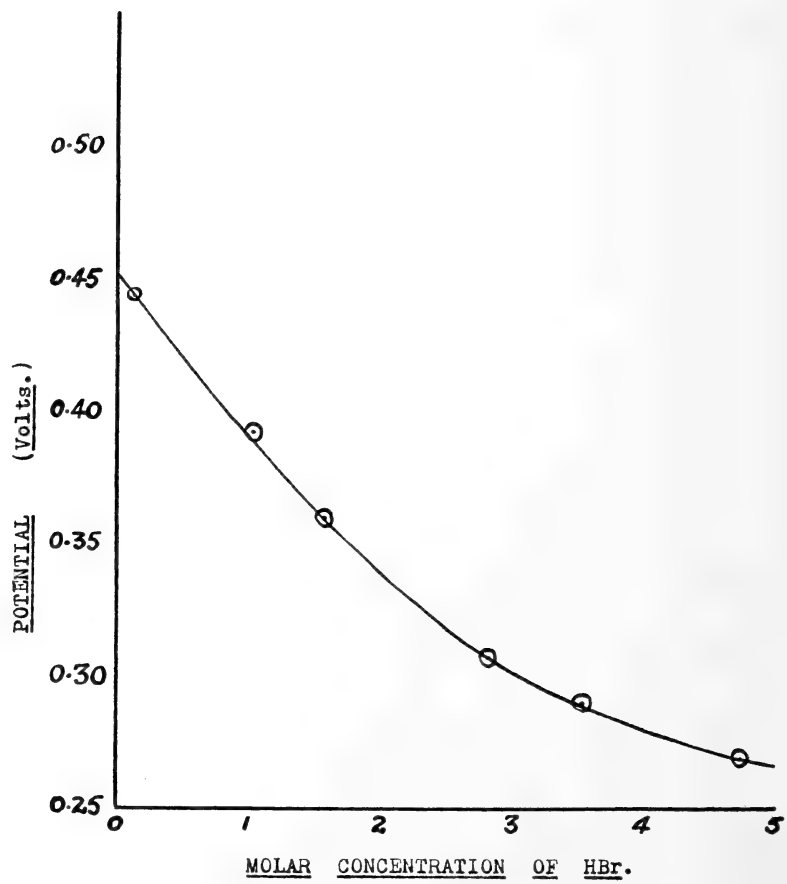

Fig. 1.

slowly. This fall of potential with increasing ionic strength is in accord with the expectation that the system is essentially cationic. This is also indirectly confirmed by the observation of Crowell and Baumbach (1938) that the potential drop during potentiometric titration in 0·1 N hydrobromic acids was greater than in 1 N acid.

Experimental.

Potassium Hexabromosmate.

This was prepared by decomposition of potassium osmyloxy nitrite with boiling concentrated hydrobromic acid as described by Wintrebert (1903). A simpler method which gave a better yield was simply to reflux osmium tetroxide with concentrated hydrobromic acid, and add excess of potassium bromide. This method is essentially the same as that of Gilchrist (1932) except that a high concentration of acid was maintained throughout to avoid hydrolysis as recommended by Mellor (1943). The identity of the black cubes and octahedra was confirmed by X-ray powder photographs.

A solution of the substance, 0·005 M in hydrobromic acid 2 N, was used.

Potassium Hexabromosmite.

Since the expected redox potential was of the order of 0·4 to 0·5 volt it was anticipated that the reduction of the bromosmate could be effected with silver wool since the potential of the system $Ag+Br' \rightarrow AgBr+e$ is $-0 \cdot 07$ volt (Latimer, 1938).

The reduction was rapid and complete, and preferable to the electrolytic method used by Crowell, Brinton and Evenson (1938).

The reduction was carried out in the burette-reservoir apparatus described by Vogel (1943) for the storage of strongly reducing solutions. The reservoir and the delivery tube leading to the micro-burette were loosely packed with pure silver wool and a 0·005 M solution of the bromosmate in 0·1 N hydrobromic acid containing the necessary potassium bromide for the reaction run in. The apparatus was then filled with oxygen-free carbon dioxide.

Reduction commenced immediately and the dark red osmate solution became lighter. At the end of 24 hours the solution had become pale straw coloured and a dense precipitate of yellow silver bromide had separated to the bottom of the vessel. From the colour of the silver bromide precipitate it was evident that reduction had not proceeded to osmium metal.

The reduction is expressed in the equation

$$K_2OsBr_6+Ag+KBr \rightarrow K_3OsBr_6+AgBr\downarrow$$

Apparatus and Experimental Procedure.

The potential measurements were carried out by the Poggendorff compensation method using apparatus similar to that described previously (Dwyer, McKenzie and Nyholm, 1944). The salt bridge, platinum electrode and carbon dioxide tube were sealed into a four-necked flask with Apiezon wax and the air displaced through the fourth neck. Some of the reduced solution was then introduced to remove adsorbed oxygen from the walls, and also that dissolved in the agar salt bridge. After 24 hours the apparatus was washed out with oxygen-free water and an oxygen-free mixture of potassium hexabromosmate 2 ml., hydrobromic acid and water to a total volume of 28 ml. introduced. Carbon dioxide was then passed for 10 to 15 minutes, and the tip of the bromosmite burette inserted whilst the gas was passing and 2 ml. of the bromosmite solution added. The whole apparatus was sealed off under carbon dioxide pressure and allowed to reach equilibrium.

Equilibrium was attained slowly, taking not less than 24 hours. Potentials fell to equilibrium at high hydrobromic acid concentrations, and rose to equilibrium at low acid concentrations.

The measured potentials are considered correct to ± 2 millivolts.

From the curve below, the extrapolated value of the couple in zero strength hydrobromic acid is 0·452 volt.

Summary.

The potentials of the trivalent-quadrivalent osmium couple have been determined in various concentrations of hydrobromic acid. From the behaviour of the potentials the system is essentially a cationic redox system. The value of the redox potential extrapolated to zero acid strength is 0·452 volt.

Acknowledgement.

The authors are indebted to Mr. J. L. Sullivan, A.S.T.C., for various X-ray powder photographs.

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THE SPECTROGRAPHIC ANALYSIS OF URANIUM.

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Introduction.

A problem arising out of the present interest in sources of uranium is that of detection and assay of the element.

Conventional chemical analysis by wet methods, use of some phenomenon associated with the radio-activity of uranium, or use of fluorescence are chief methods in vogue, although less obvious methods can be employed.

So far as is known, spectrographic methods have not been applied to uranium previously, although wave-length tables have been published (Meggers and Kiess, 1920 *et al.*). Actually only the most persistent lines are of interest in analysis. Pollok (1905–8) established these for the spark spectrum of uranium chloride, but similar work for the arc spectrum has not been reported.

The purpose of this paper is to record what has been achieved in this direction here, and to discuss in broader outline the whole problem of analysis of uranium by its arc spectrum.

Equipment Used.

Conventional electric arcs in air and on 220 volt D.C. supply served as light sources. Currents were 10 amps. for graphite and 4 amps. for copper electrodes.

Spectrograms were obtained with a Hilger E179 spectrograph (FD =100 cm.) fitted with either quartz prism or plane grating on speculum having 24,000 lines at 10,800 per inch (Grayson, 1918).

Selection of Uranium Lines.

This was necessarily the first step. Its immediate purpose was to present in compact form all lines likely to be of use for uranium analysis under recommended conditions of arcing. This has been done quite independently of the intensity data in the M.I.T. tables, although good general agreement is found to exist.

Spectrograms used were from arcings of pure uranium acetate on graphite, or uranium oxide on copper (to avoid CN. bands). Light was taken from the middle 2 mm. of a 5–6 mm. arc. Subsequently when it was found that the cathode layer yielded higher sensitivity, the list was revised, taking light from the cathode layer, but no appreciable alteration was called for.

Lines were selected primarily by their intensity as estimated from the spectrograms. The strongest lines in each region between 8,000 and 2,500 Å.U. were included rather than the 124 photographically strongest lines in the spectrum. Choice of working region may be limited in practice by available equipment. This list has been compiled on the principle that all regions might be required under special circumstances.

Diffuse lines were excluded but several close groups were included. Taken separately the lines might not have warranted inclusion, but with medium dispersion equipment the blend appears intense.

Finally, the actual persistences of these lines were compared by arcing a uranium ore continuously while the plate was racked at regular intervals (corresponding to the "jumping plate" technique of eclipse spectrography. The method is sometimes used in spectrographic analysis for concentrating refractory trace elements.) As the sample volatilises the lines decrease in intensity and can be tabulated in order of disappearance. No detail of this will be recorded here, as the relative persistences by this method will involve the spectral characteristic of the photographic plate used, and will have no absolute significance. However, a good corroboration of the lines selected by intensity alone was obtained.

The selected group, comprising 124 uranium lines, is recorded in Table 1.

Note on the "Raies Ultimes".

From the position of uranium in the periodic table it can be predicted that the strongest line of the uranium arc spectrum will appear somewhere between 4,500 and 3,500 Å.U. Fortunately the strongest lines of some 70 elements are established. The former statement is based on an extrapolation of the general trend in wave-length observed from left to right and also from top to bottom of the periodic table for those elements in which the strongest lines are established. The wave-length 4825·91 is accepted for radium which is the only element of the seventh period whose first spectrum has been analysed. It is also assumed that actinium resumes building subshell *d* electrons ($6d$) after completing the $7s$ subshell with radium ($7s_2$) (cf. scandium, yttrium, lanthanum, in the three long periods, for which this process is confirmed).

Now it is apparent from casual inspection that the spectral region 4,500 to 3,500 Å.U. is in fact decidedly richer in medium strength lines than any other region and also that the strongest lines with few exceptions lie in this region. A further classification has therefore been attempted.

This includes the 25 uranium lines reckoned to be the photographically strongest and most persistent in the spectrum. These are the lines which should be consulted for ultimate sensitivity. They are distinguished in Table 1 by an asterisk before the wave-length.

It can be stated with reasonable confidence that the "raies ultimes" will be among these lines. However, to identify them is more difficult. This requires a knowledge of accurate relative intensities, relative presistences, or the energy states of the atom. None of these is available for uranium.

"Raies ultimes" published by Pollok (1905–8) as established by his spark spectra are apparently incorrect for arc conditions. He reported the lines 4241·669, 3672·579, 3552·172 Å.U. (M.I.T. wave-lengths) as the most persistent in dilute solutions of uranium chloride and these lines are still generally accepted. However, in the arc spectrum both 3672 and 3552 Å.U. are very weak lines, although 4241 Å.U. is among the 25 strong lines. This is confirmed by Kayser and Ritschl's "Hauptlinien", which does not even include the two weak lines. Furthermore, it seems very improbable that the strongest lines of the singly ionised atom could possess such long wave-lengths, if we may judge from the trend in wave-lengths of the elements whose second spectra have been analysed, in which case it is difficult to accept them as correct for the spark.

Pollok's D.C. spark conditions have not been accurately simulated here, but spectrograms have been taken of an A.C. 13,000 volt condensed spark, using 0·008 mfd. and enough inductance to remove air lines, between pointed graphite electrodes saturated with uranium chloride solution. As expected, a consider-

TABLE I.

Uranium Lines.	Interfering Lines.	
7970·46	Si	7970·91
	Si	7970·26
7881·94	None	
7784·13	None	
7533·91	Fe II	7533·42
7425·50	Si I	7424·63
7128·91	None	
7074·81	None	
6826·93	Mn	6827·12
6449·167	Co I	6450·239
	Ca I	6449·810
	Cu II	6448·49
6395·446	Co I	6395·195
5915·398	Co I	5915·539
	Si	5914·7
5621·524	Si I	5622·22
	Fe	5621·28
5581·610	Ca I	5581·969
5581·230		
5580·819		
5564·187	Fe I	5563·604
5527·848	Mg I	5528·461
5511·501	None	
5492·970	Fe I	5493·511
5481·223	Fe I	5481·459
	Ti I	5481·431
	Mn	5481·396
	Fe I	5481·252
	Fe I	5480·873
5475·725	Fe	5476·295
5311·881	Al II	5312·32
5280·389	Fe	5280·360
	Al II	5280·21
5247·749	Co I	5247·932
5184·587	Fe I	5184·292
5160·326	None	
5117·249	Mn	5117·937
*5027·398	Fe	5028·137
	Fe	5027·212
	Fe I	5027·136
*5008·222	None	
4899·294	Ti I	4899·912
	Al II	4899·64
	Co I	4899·522
	Al II	4898·76
4847·660	Ca I	4847·296
4819·544	Si	4819·57
4772·701	None	
4769·260	None	
4756·803	Co I	4756·725
4731·599	Fe II	4731·492
4722·726	Ti I	4722·616
4689·074	None	
4666·856	Cu II	4667·297
	Al II	4666·8
	Mn	4666·49
4646·603	None	
4631·620	Al II	4631·5
	Ca	4631·39
	Si	4631·22
4627·079	Mn	4626·544
4620·219	Mn	4620·21
4603·665	None	
4573·687	Mn	4573·635
*4543·632	Mn	4544·414
	Co I	4543·812
4515·280	Fe II	4515·345
*4472·335	Mn	4472·792
	Fe	4472·721
4393·588	Ti I	4393·925
	Mn	4393·37
	Ca	4393·168
*4362·262	None	
4362·05		
*4341·688	Ca	4341·110
	V I	4341·013
*4282·028	Fe I	4282·406
	Ti I	4281·376
4246·261	Ca	4246·095
	Fe	4246·090
*4244·372	None	
*4241·669	Cu I	4242·26
*4171·591	Fe	4172·127
	Cu II	4171·854
	Fe	4171·700
4156·652	Mn	4157·019
	Fe I	4156·803
	Fe I	4156·681
*4153·976	Fe	4154·108
	Fe I	4153·910
	Ca	4153·65
	Cu II	4153·623
*4116·097	Si	4116·15
	Ca	4116·095
*4090·135	Mn	4090·606
	V I	4090·579
	Fe I	4090·077
	Mn	4089·938
*4063·119	Fe I	4063·597
	Mn	4063·528
	Cu I	4063·293
	Fe I	4063·284
	V I	4062·72
	Cu I	4062·698
*4050·039	Fe	4049·87
	Mn	4049·431
*4042·752	None	
3985·795	Fe I	3986·172
3966·567	Fe I	3966·629
	Fe I	3966·518
*3943·820	Al I	3944·032
	V I	3943·664
	Fe	3943·594
	Fe I	3943·348
*3932·026	Fe	3932·27
	Ti II	3932·017
3890·364	Fe	3890·844
	Fe I	3890·390
	Mg I	3890·241
	Fe	3890·237
	V I	3890·184
3871·042	V I	3871·078
	Fe	3870·810
	Si	3870·64

TABLE 1.—*Continued.*

Uranium Lines.	Interfering Lines.	
3871·042	Ca I	3870·506
3865·923	Al II	3866·160
	Mn	3865·66
	Fe I	3865·526
*3859·580	Fe I	3859·913
	Ca	3859·675
	Al II	3859·33
	Fe I	3859·216
	Mg I	3859·211
3854·655	Mg I	3854·538
3854·230	Mg I	3854·117
	Fe	3853·824
3839·632	Mn	3839·777
	Fe	3839·630
	Fe	3839·259
3831·465	None	
3811·999	Co I	3812·470
	Fe I	3811·895
3782·841	Ca	3783·24
	Fe	3782·612
	Fe I	3782·456
3731·453	Fe	3731·378
3701·745	Co	3702·243
3701·522	Fe	3702·031
	Si	3702·01
	Mn	3701·730
	Ca	3701·15
	Fe I	3701·090
*3670·072	Ca	3670·21
	Fe	3670·071
	Fe I	3670·028
	Fe	3669·757
*3659·159	Fe I	3659·521
	Cu I	3659·353
3638·200	Fe I	3638·298
	Fe I	3637·866
*3584·879	Fe I	3585·320
	Co I	3585·160
	Fe I	3584·790
	Fe I	3584·663
*3566·598	Fe I	3567·038
	Fe	3566·582
	Fe I	3566·311
*3514·615	Fe	3514·626
3507·344	Fe II	3507·397
3507·051	Cu I	3507·38
	Fe	3507·170
3500·077	Cu I	3500·324
	Ca	3500·26
	Fe II	3499·877
*3489·371	V I	3489·467
	Co I	3489·402
	Cu I	3488·858
3466·30	Fe I	3466·500
	Mn II	3466·336
	Fe I	3465·863
3459·917	Mn II	3460·328
	Mn II	3460·018
	Fe I	3459·918
	Fe	3459·740
3435·53	None	
3435·20		
3424·557	Ca	3424·92

Uranium Lines.	Interfering Lines.	
3424·557	Co I	3424·506
	Fe I	3424·288
3390·389	V I	3390·765
	Ti I	3390·682
	Co I	3390·403
3337·79	Cu I	3337·844
	Fe	3337·666
3305·926	Fe I	3306·354
	Fe I	3305·971
3291·335	Fe I	3290·989
	Mn	3290·988
3270·124	Ca	3270·502
	Mn	3270·351
	Fe II	3269·772
3232·157	None	
3206·227	Ca	3206·10
3206·049		
3151·084	Fe	3151·351
	Ca I	3151·280
	Cu II	3151·049
	Fe	3151·005
	Ca I	3150·738
3119·348	Ca	3119·671
	Fe	3119·667
	Fe	3119·494
3111·621	Fe	3112·081
	Fe	3111·821
	Fe ,	3111·684
3102·39	Fe	3102·872
	Fe	3102·638
	Co I	3102·407
	Fe	3102·361
	Ca	3102·359
	Fe	3102·144
3057·91	Fe	3057·790
	Fe	3057·65
3044·159	Mn	3044·567
	Cu I	3044·028
	Co	3044·005
	Mn	3043·77
	Mg I	3043·75
3024·385	Ca	3024·70
	Al II	3024·074
	Fe I	3024·033
3022·207	Cu I	3022·613
	Co I	3022·362
2984·613	Fe I, II	2984·830
	Fe	2984·575
2982·740	Ca I	2982·89
	Cu I	2982·765
2967·894	Mg II	2967·87
2941·919	Mg I	2942·11
	Ti I, II	2941·995
	Fe	2941·75
2908·275	Mn	2907·993
	Ca	2907·90
2906·913	Mn	2907·216
2906·798	Fe	2906·97
	Fe	2906·61
	V II	2906·457
	Fe	2906·421
2889·627	Fe	2889·992
	Fe	2889·88

TABLE 1.—*Continued.*

Uranium Lines.	Interfering Lines.		Uranium Lines.	Interfering Lines.	
2889·627	V II	2889·621	2683·279	Mn	2683·016
	Mn	2889·58	2645·47	Si	2645·59
2882·741	Cu I	2882·934		Fe I	2645·427
	Mn	2882·902		Fe	2645·330
	V II	2882·501		Fe	2645·191
2865·679	Fe	2865·87	2635·528	Fe I	2635·808
2821·122	Mn	2821·452		Mn	2635·600
	Fe	2821·01		Fe II	2635·393
	Fe I	2820·809	2597·689	Fe II	2598·028
2793·937	Fe	2794·16		Fe II	2597·943
	Fe II	2793·888		Fe	2597·828
2754·155	Fe	2754·426		Mn	2597·510
	Ca	2754·18	2591·252	Fe II	2591·543
	Fe I	2754·037		Mn	2591·424
	Fe	2753·81		Fe	2591·256
2733·967	Fe I	2734·273		Mn	2591·229
	Fe I	2734·004	2565·406	Fe	2565·708
	Fe I	2733·584		Al II	2565·68
	Mg I	2733·57		Ca	2565·48
2683·279	Al II	2683·280		Fe	2565·46
	V I	2683·091		Mn	2565·223

able increase of numerous short-wave lines 3,000—2,000 Å.U. occurred, but the lines 3672 and 3552 Å.U. were not increased very much.

The under-water spark spectrum between uranium electrodes should indicate the " raies ultimes " as the lines most readily reversed.

PROBABLE INTERFERING LINES.

The chief consideration deciding the usefulness of a line selected because of its intensity, is that of possible interference with lines known to be present in the substance to be arced. Such data as can be listed concerning this must necessarily be rather arbitrary in so far as ores vary in composition. However, experience has been gained with ores from Mt. Painter, South Australia, and special attention will be given to these.

Qualitative spectro-chemical analyses of Mt. Painter ores always revealed well-developed spectra of Al, Ca, Cu, Fe, Mg, Mn, Si and sometimes weak spectra of Ag, Co, Ti, V, with occasional traces of other elements. Therefore in considering interferences all lines of the first group will be admitted, but only strong lines of the second group.

It is a moot point up to what wave-length separation a line can be regarded as interfering. Obviously it depends on the resolving power and dispersion of the spectrograph, but also on several factors which are difficult to estimate. For the purpose of tabulation here, lines will be admitted if within 1·0 Å.U. at 8000 Å.U., 0·75 Å.U. at 6000 Å.U., 0·5 Å.U. at 4000 Å.U. and 0·25 Å.U. at 2000 Å.U.

Interfering lines are catalogued in Table 1. Wave-lengths are taken fiom " M.I.T. Wave-length Tables ".

Actually many of these lines are weak and may cause no trouble. However, 44% of the lines belong to iron, and because of the concentration of iron in Mt. Painter ores, the majority of these lines will in fact be recorded. The presence of appreciable iron is therefore to be regarded as always imposing the severest restrictions on choice of uranium lines.

Of the 25 stronger lines listed, only four have no interfering lines recorded: 5008, 4362, 4244, 4042 Å.U., and of these the latter two are to be preferred. This does not mean that no other strong lines are useful, but that, in general, higher resolution is necessary.

Absolute Sensitivity in Arc Column and Cathode Layer.

Electric arcs and sparks are distinctly inhomogeneous as regards excitation conditions. For spectroscopic work this imposes the necessity for always taking light from the same region of the gap.

Measurements of the absolute sensitivity of uranium have been made here for both arc column and cathode layer. One-quarter-inch Hilger graphite electrodes were prepared with shallow craters over which a collodion skin was formed (to prevent penetration of the solution). 0·1 cc. of pure uranium nitrate solution was dropped into each crater by graduated pipette. Solutions were graded so that the quantity of uranium introduced ranged from 10^{4-}–10^{-1} mgm.

Two sets of spectrograms were obtained from such electrodes (*a*) charged electrode lower and positive, arc column projected on slit, (*b*) charged electrode lower and negative, cathode layer projected on slit. Uranium lines appeared to decline regularly in density, but it was found difficult to interpolate between steps, i.e. to decide whether a line was about to disappear. In any case this is rather subjective, and since it also depends on the spectrograph, contrast in the plate, etc., it seems sufficient to quote the order of magnitude only.

It may be said that 10^{-3} mgm. of uranium can be detected in the cathode layer and about 5×10^{-3} mgm. in the arc column. Both are conservative figures. The impression was gained that a somewhat smaller quantity might be detected by further refinement of technique.

Sensitivities were similarly determined for $\frac{1}{4}$ in. copper electrodes chiefly to avoid the CN. band system. However, an appreciable continuous spectrum appeared. The cathode layer was also less distinct. Results did not differ much from those obtained for graphite. The figure 10^{-3} mgm. is probably about the limit of detection likely to be reached by spectrographic methods.

However, all such figures should be treated with some reserve. The writer knows from experience in determining sensitivities of other elements in several different base solutions just how much the result can be influenced by the medium.

Spectrograms were also taken of standard mixtures and ores to find the least detectable percentage of uranium.

First experiments were made with pure quartzite samples medicated with UO_3 increasing in convenient steps. Arcings were made on graphite and copper, using light from the cathode layer. Samples up to 20 mgm. were used. These gave spectra which were not very complex and interferences were comparatively few. For instance the weak iron doublet 3670·071, 3670·028 Å.U. did not appear, permitting use of the strong uranium line 3670·027 Å.U. (certainly one of the strongest lines in the spectrum). Under these circumstances a detection of 0·05% uranium proved practicable.

Tests were then made with actual ores taken chiefly from the Mt. Painter deposits, which had been chemically analysed and which covered the range 0·05% to 0·5% uranium. With these the full complexity due to interfering elements was experienced. As above, arcings were made on graphite and copper, using the cathode layer, but here again no significant difference between the amounts detected could be claimed. Apparently the advantage possessed by copper in being able to use certain strong lines lying in the CN. band region is offset by a slightly lower sensitivity inherent in the copper arc and by its considerable background.

A conservative statement is that the cathode layer technique certainly permits detection of 0·1% uranium, and may achieve 0·05% or even less under favourable conditions.

Discussion of Apparatus and Technique Suitable for Uranium Analysis.

The spectrographic analysis of uranium demands rather more attention to instruments and technique than is generally necessary, primarily because uraniferous ores show very complex spectra, but also because the spectrum contains no very strong lines, so that detection and estimation may be required at or near the limit of sensitivity.

It seems worth while, therefore, to devote some attention in this article to the instrumental requirements, with special reference to the practice employed here.

The spectrograph must be able to photograph the region containing strongest lines, namely 4500—3500 Å.U., and yield sufficient resolving power and dispersion to isolate at least some of the analytically important lines. Also the greater the dispersion, the weaker the background relative to lines. The intense continuous spectrum observed with uranium is unimportant when uranium is present in trace amounts, but all arcs give an appreciable background due to incandescent particles in the flame. The frequent occurrence of band spectra advises a dispersion sufficient to distinguish superposed atomic lines, e.g. SiO_2 bands occur in many ore spectra and the graphite arc involves the intense CN. system.

A calculation of the requisite resolving power of a spectrograph for uranium analysis involves many factors. For instance, Table 1 yields the least difference of wave-length which must be resolved for Mt. Painter ore to avoid interferences, but to identify this with the theoretical resolving power found from the grating or prism constants is quite inadequate. The fact that slits are finite, lines broadened, and photographic emulsions possess grain and are susceptible to halation, all reduce the observed resolution and the effect of most of these may be calculated or estimated by well established methods.

Fortunately Doppler breadths of uranium lines, even at arc temperatures, are small on account of the high atomic weight of uranium, but interfering lines are unpredictable, e.g. CuI 4242·26 Å.U., which may interfere with the useful line U 4241·669 Å.U., has a natural breadth of 0·41 Å.U.

It has been noted that only four of the 25 strong lines are free from interference within the prescribed wave-length tolerance, i.e. at about 4000 Å.U. any spectrograph capable of separating clearly 0·5 Å.U. can be used. In the writer's opinion to achieve this the spectrograph should have a theoretical resolving power of about 0·2 Å.U. Best results were obtained here using the grating. The quartz prism system with a resolving power of 0·52 Å.U. is inadequate, but useful results have been obtained with this by using weaker lines in the ultra-violet. Something of a drop in sensitivity is incurred, but not as much as might be expected, because the superposed continuous spectrum falls off rapidly in the ultra-violet, and it is this background which often imposes the limit to sensitivity at longer wave-lengths. The prism also makes better use of the light as regards intensity. A two-prism glass Littrow system now being tried here promises to be best for uranium work. This has adequate resolving power at 4000 Å.U. but cannot be used in the ultra-violet.

Setting up the condensing system has been found to be fairly critical. Mirrors proved better than lenses.

For qualitative analysis, an aluminised spherical concave mirror 10 cm. diameter and 20 cm. focal length focuses the arc on the slit (Fig. 1). A stop

prevents direct rays entering the instrument. The mirror is holed (2·5 cm. diameter) to permit projection of an image of the arc on a fiducial mark on the wall—a conventional method of locating the source.

For quantitative analysis the mirror projects an image of the arc on a diaphragm having an aperture variable in size and position (Fig. 2). This permits light to be selected from the source as desired. An image of this aperture is formed by a simple quartz lens placed in front of the slit, at a point near the prism of the spectrograph, thus uniformly illuminating the slit. Lines are now uniform in density and suitable for microphotometry. A step sector can be inserted if required between lens and slit.

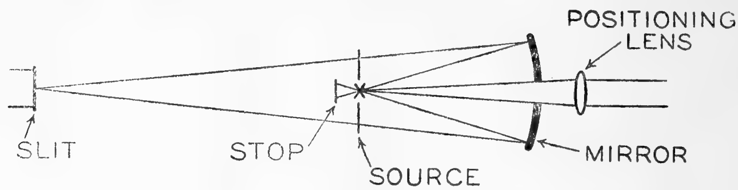

Fig. 1.

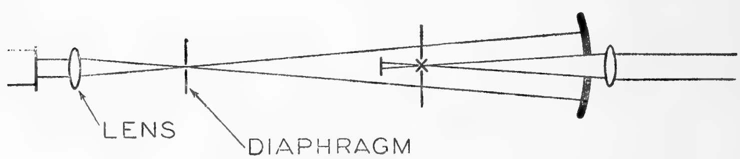

Fig. 2.

The advantage of mirror over lens is one of achromatism. A clearly defined cathode layer can be secured across the whole spectrogram.

Of the flame, arc and spark sources, only arc excitation has been studied here. The flame temperature is too low for uranium and the spark would be limited chiefly to solutions. For both qualitative and quantitative analysis, the cathode layer arc is recommended. Samples of 10–20 mgm. have been used here, but smaller quantities could probably be substituted. Strock recommended 1–3 mgm., but no doubt had in mind elements of far higher sensitivity. However, too much sample does tend to destroy the cathode layer. This point requires further investigation.

For quantitative analysis the internal or external standard principles are suitable. Iron lines are abundantly available for line pairs. However, iron content is apparently not sufficiently constant in the Mt. Painter field to use iron as internal standard without correction. Two courses lie open: (*a*) to use uranium-iron pairs giving uranium content relative to iron and determine iron by some other method, (*b*) to add an external standard. A number of suitable heavy elements suggest themselves.

General Remarks.

It is not the purpose of this paper to convey the impression that spectrochemistry provides a perfect method for uranium analysis. Rather it aims at providing the hitherto lacking experimental data which will permit a comparison of the utility of the method with, say, chemical analysis or the Geiger tube.

The assayer is likely to be interested in two types of work: (1) large-scale preliminary survey of suggested fields (of the kind recently undertaken in parts of Australia), (2) accurate analysis of promising ore types.

He will ask what advantages and disadvantages attend the use of the spectrograph for such work.

Sensitivity. A high sensitivity is one of the much quoted attributes of spectro-chemistry, but it is not shared by uranium. 10^{-3} mgm. is low in comparison with many other elements. In Mt. Painter ores this corresponds to a detectable limit of about 0·1%. Chemical methods can certainly reach 0·01%. Geiger sensitivity is still greater. On the other hand, spectro-chemical methods will certainly be adequate for all ores likely to be workable from an economic standpoint.

Speed and Accuracy. Numerous metallurgical applications have established that spectrographic methods attain highest speed and accuracy when applied to series of systematic analyses. (1) and (2) involve just this, but there is a difference which lends special favour to (1). A sacrifice of accuracy to achieve greater turnover of results is legitimate here where the aim is only a first classification according to richness—quite often, in fact, merely " accept or reject ".

Conventional chemical analysis does not lend itself to this type of problem. There is no flexible relationship between speed and accuracy which would allow a compromise to be effected according to the demands of either one, and unfortunately the labour and time involved for a uranium analysis is excessive.

On the other hand, spectro-chemistry lends itself to successive refinement in accuracy at the expense of some speed (or *vice versa*) just by a modification of the same basic technique. For instance in (1) it may be sufficient to distinguish between 0·1%, 0·3% and 0·5%. The spectrograph can achieve this with simple technique. Subsequently for (2) a revised technique may achieve a higher accuracy.

The ultimate accuracy of the spectrographic method is probably about $\pm 2\%$ of the uranium content over the range 0·1–10% uranium, under favourable conditions.

Chemical analysis is unquestionably better suited to (2) than (1). It is also more accurate than spectro-chemistry with this kind of problem.

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VOLUME LXXX

PART IV

THE MECHANISM UNDERLYING THE FORMATION OF AQUEOUS NEGATIVE BINARY HOMOAZEOTROPES.

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The Scots College, Sydney.

With three tables.

Manuscript received, October 9, 1946. Read, November 6, 1946.

INTRODUCTION.

When water containing less than 20·2 per cent. by weight of hydrogen chloride is distilled at normal atmosphere pressure, the first runnings are more dilute than the original solution, and the concentration of the residual liquid rises until it reaches that figure, when it distils unchanged. The resulting aqueous acid is often called *constant boiling hydrochloric acid.* Similarly, if the original acid contains more than 20·2 per cent. by weight of hydrogen chloride, the first runnings are still more concentrated and the residual acid becomes more dilute until it reaches that figure, when the constant boiling acid distils unchanged.

In both the foregoing cases the boiling points of the solutions rise until the boiling point of the constant boiling mixture is reached, viz. 108·584° C. Thus the constant boiling hydrochloric acid has the highest boiling point of all aqueous solutions of hydrogen chloride.

Constant boiling solutions which have maximum boiling points are referred to by W. Swietoslawski as *negative homoazeotropes.* The sign is used to distinguish them from constant boiling solutions which have minimum boiling points, such as the well-known ethanol-water solution. According to Swietoslawski the term *azeotrope* was introduced in 1911 by J. Wade and R. W. Merriman to refer to a mixture which distils unchanged, while Swietoslawski applies the prefix *homo-* to remind us that we are dealing with mixtures forming only one liquid phase. Since constant boiling hydrochloric acid has water as one of its two components, it is an example of an aqueous negative binary homoazeotrope.

HISTORICAL.

Negative binary homoazeotropes of which water is a component have been known from the days of John Dalton, whose name heads the chronological list given in M. Lecat's bibliography of azeotropy. Until 1860 they were believed to consist of pure hydrates. This view rested on their apparent conformity with the law of definite proportions and on the then widely held opinion that a liquid which distilled unchanged at a fixed temperature must be a chemically homogeneous substance. Further, the analyses of the then known aqueous negative binary homoazeotropes corresponded closely with the atomic ratios in current use. Thus A. Bineau regarded constant boiling hydrochloric acid as $HCl+16HO$, and constant boiling nitric acid as HNO_6+3HO, while E. Mitscherlich preferred HNO_6+4HO. Bineau concluded that the constant boiling hydrofluoric, hydrobromic and hydriodic acids were tetra-, deca- and undeca-hydrates respectively.

In 1860 H. E. Roscoe and W. Dittmar found that the percentage of hydrogen chloride in constant boiling hydrochloric acid decreased when the pressure under which it was prepared was increased, and that the boiling points of hydro-

chloric acids of constant composition all lie about 9° higher than the boiling points of water under the same pressure. They wrote as follows :

" We are, therefore, induced to admit the existence of certain attractions between the molecules of hydrochloric acid gas and water, which, if they do not give rise to definite chemical combinations, are at any rate essentially different from the attractions exerted between water and the other even the most soluble gases.

" We may shortly explain the results of our experiments by supposing that certain definite chemical compounds of water and hydrochloric acid exist, but that they undergo a gradual alteration with variation of temperature, so that, for every temperature, a definite combination exists, which at this temperature remains unchanged by exposure to a current of dry air, and may be boiled without changing its composition, if the pressure is such that the liquid boils at this same temperature."

Thus was born what may be termed the molecular attraction theory of azeotropy, a theory which has persisted to our present day.

Roscoe's shaken belief in the hydrate theory was further weakened by his subsequent careful examination of the constant boiling aqueous solutions of nitric, sulphuric, hydrochloric, hydrobromic, hydriodic and hydrofluoric acids. In 1861 he wrote :

" Although the laws which regulate the vaporization of mixed liquids are as yet far from being understood, it is easy to see that the relations between the several tensions and the proportions by weight of the two or more constituents may be such that, at a given temperature of ebullition, the composition of the vapour is identical with that of the liquid. As soon as this point is reached, the mixed liquid boils at a constant temperature without undergoing any change of composition, and in this respect does not differ from a uniform combination."

In the same year Roscoe discovered the negative homoazeotrope of perchloric acid with water and was strengthened in his opinion " that the phenomena of constant composition and fixed boiling point are . . . dependent mainly on physical rather than upon chemical attractions."

During the following years the views on the underlying reason for the phenomena seem to have swayed between the solvation and molecular attraction theories. A compromise appeared to be possible by regarding solvation and molecular attractions as similar in kind but different in degree. Thus in 1945 Swietoslawski wrote that in the case of negative homoazeotropes the forces of mutual attraction between different molecules, A and B, are greater than that between identical molecules, thus restating a view which has been widely held. Swietoslawski continued by pointing out that numerous examples of negative azeotropes occur in which the formation of associated molecules or even chemical compounds seems very probable, but that there are still a number whose existence cannot be explained by a chemical reaction between the components. He opined that the association of molecules may exist in the same manner as in cases of one-component liquid systems.

Swietoslawski's views seem to agree in essence with those of J. H. Hildebrand, which are expressed in the following quotation :

" Negative deviations from Raoult's law result from tendency towards chemical union, and when this is sufficiently marked to counteract any difference in boiling points of the pure components it may give rise to a . . . maximum in the boiling point curve. The following cases of negative deviation have already been mentioned, chloroform-acetone ; chloroform-ether. The former gives a maximum boiling point . . . while the latter by reason of the difference of 26·4° in the boiling points of the pure constituents, is not able to show a maximum."

Table 1, constructed from data given by S. Young, shows six negative homoazeotropes whose components differ in boiling point by more than 26·4 centigrade degrees.

TABLE 1.

Negative Homoazeotropes whose Components Differ in Boiling Point by More than 26·4 Centigrade Degrees.

	b.p. ° C.		b.p. ° C.	Difference.
Hydrogen chloride ..	−84	Water	100·00	184
„ bromide ..	−73	„	„	173
„ iodide ..	−34	„	„	134
„ fluoride ..	19·4	„	„	80·6
„ chloride ..	−84	Methyl ether ..	−23·65	60·35
Formic acid	100·7	Picoline, α ..	134	33

A Suggested Mechanism to Account for the Formation of Aqueous Negative Binary Homoazeotropes.

In reviewing the problems of electrolytic dissociation, S. Glasstone stated in 1945 that:

" In all electrolytes, except perhaps for very dilute solutions of certain univalent salts, e.g. potassium and sodium chloride, undissociated molecules are present: it is uncertain, however, whether these are merely ion-pairs held together by electrostatic (Coulomb) forces, in which case the electrolyte may be said to be completely ionized but incompletely dissociated, or whether there are actually present some unionized molecules in which the radicals are held together by covalent linkages. As already stated, the law of mass action should be applicable in either case . . . "

On the basis of this view the underlying reason for the formation of the aqueous negative binary homoazeotropes may be as follows:

Let M^+A^- be a strong electrolyte which when pure has a boiling point lower than $(100+\theta)^\circ$ C., where θ is not more than a few degrees. The addition of a small quantity of M^+A^- to water will produce ions M^+ and A^-, which may or may not be hydrated. It is generally believed that the vapour above a boiling electrolytic solution does not contain ions; hence the ions M^+ and A^- (or their hydrates) are considered as being non-volatile solutes and, as such, raise the boiling point of the solution above 100° C. When still more of the compound M^+A^- is added, the boiling point of the solution rises above $(100+\theta)^\circ$ C. However, as the concentration of the solution increases there will be, according to the law of mass action, an increasing quantity of volatile undissociated molecules of M^+A^-. The effect of the presence of this volatile constituent will be to lower the boiling point of the solution, and this effect is opposed to that of the ions. Continued addition of M^+A^- to the solvent will therefore raise the boiling point of the solution by decreasing amounts, and eventually will lower the boiling point when such additions of M^+A^- shall give to the solution so much volatile M^+A^- that the effect of the ions is counteracted.

Aqueous solutions of acids may be represented by the equation

$$HX+nH_2O \rightleftarrows [H(H_2O)_m]^+ + [X(H_2O)_{n-m}]^-$$

The reactants on the left-hand side are volatile; those on the right-hand side are here regarded as involatile. If to a solution of HX in water whose concentration is less than that of the homoazeotrope be added a further small quantity of HX, it is here supposed that the concentrations of undissociated HX and of

its ions are both increased, but that the effect on the boiling point due to the increase in the concentration of HX is less than that due to the increased concentration of the ions, owing to the tendency of HX to dissociate considerably in solution. If a small quantity of HX be added to its solution whose concentration is greater or equal to that of the azeotrope, it is suggested that, owing to the small tendency for HX to dissociate in such more concentrated solution, the concentration of undissociated HX is increased more than is that of its ions, hence the boiling point of the solution is lowered.

Application of the Mechanism to Known Aqueous Negative Binary Homoazeotropes.

Young's list of negative binary homoazeotropes includes seven cases in which one component is water, the other component being in every case a relatively volatile acid. This is shown in Table 2.

Table 2.

Substances Listed by S. Young as Forming Aqueous Negative Binary Homoazeotropes.

Name of Solute.	b.p. ° C.	Homoazeotrope.		Observer.
		Percent. Solute by Wt.	b.p. ° C.	
Nitric acid	86·0	68	120·5	Roscoe.
Hydrochloric acid	−84	20·22	108·584	Bonner.
Hydrobromic acid	−73	47·5	126	Carriere.
Hydriodic acid	−34	57	127	Roscoe.
Hydrofluoric acid	19·4	37	120	Roscoe.
Formic acid	99·9	77·5	107·1	Roscoe.
	100·75	77·5	107·3	Lecat.
Perchloric acid	110·0	71·6	203	Roscoe.

1. *Strong Acids.*

Nitric, hydrochloric, hydrobromic and hydriodic acids are all strong electrolytes having boiling points below that of water, and therefore the proposed mechanism is applicable to these cases without comment. In dilute solutions they are almost completely dissociated and the ions are expected to raise the boiling point of the solutions above that of water. In concentrated solutions the presence of volatile undissociated molecules or ion-pairs lowers the boiling point.

Young has assumed that the boiling point of pure anhydrous perchloric acid is 110·0° C., but a careful perusal of Roscoe's paper from which Young derived his data casts doubt on this. Roscoe reported that impure crystallized perchloric acid monohydrate undergoes effervescent decomposition at 110° C., and that pure perchloric acid begins to decompose at 75° C., while at 92° C. a dark red liquid containing 94·77 per cent. $HClO_4$ distils over, followed by explosive decomposition. A search of subsequent literature shows that later work on the distillation of pure perchloric acid has always been carried out at low pressures, and so the true boiling point of pure perchloric acid at 760 mm. must be regarded as unknown. Further, P. C. L. Thorne and E. R. Roberts (1943) state that perchloric acid is not a simple substance but an equilibrium mixture of the acid with Cl_2O_7 and water, which forms a hydrate with the perchloric acid.

The distillation of sulphuric acid was investigated by J. C. G. de Marignac, and his results were confirmed by Roscoe. A negative homoazeotrope is formed having a composition which was expressed between 98·1 and 98·8 per cent. HSO_4, and having a boiling point of 338° C. When still more concentrated acid was distilled it yielded sulphur trioxide, which was seen in the receiver, the residual acid being the homoazeotrope. Likewise, more dilute acid yielded the same homoazeotrope. The homoazeotrope was said by Marignac to distil without further change. In the light of these findings it is therefore suggested as reasonable to regard sulphuric acid of any concentration as having as its components sulphur trioxide and water. To insist otherwise because an actual solution of sulphuric acid contains little or no sulphur trioxide as such is analogous to refusing to regard the components of a very dilute hydrochloric acid as water and hydrogen chloride. Highly concentrated sulphuric acid yields sulphur trioxide when distilled; very dilute sulphuric acid yields water when distilled. Also, Thorne and Roberts state that the addition of SO_3 to 100 per cent. H_2SO_4 does not break the continuity of many of the curves showing the variation of important physical properties with concentration. It therefore follows that the pure components which produce the mixture of substances which comprise sulphuric acid of all concentrations may be regarded as water and sulphur trioxide, and the boiling point of the latter is lower than 100° C.

2. *Weaker Acids.*

W. F. K. Wynne-Jones and L. J. Hudleston have pointed out that whereas hydrofluoric acid is a typical weak electrolyte at concentrations less than 0·02 N., at greater concentrations the acid resembles a transitional electrolyte, while above 0·4 N. the activity of the hydrogen ion is materially greater than the hydrogen ion concentration. The considerable concentration of ions which occurs in 37 per cent. by weight of hydrogen fluoride in water can therefore account for the formation of the negative azeotropic solution.

Formic acid is a weak acid, having a dissociation constant of $1 \cdot 76 \times 10^{-4}$ at 25° C. The boiling point of the pure anhydrous acid has been given as 99·9° C. by Roscoe, 100·75° C. by Lecat. It is certainly so close to 100° C. that the presence of undissociated molecules of formic acid in water should have little effect on the boiling point of water. The formation of the relatively small concentration of ions by the weak acid can therefore provide sufficient involatile constituents to raise the boiling point of the solution. Hence on account of the closeness between the boiling points of the pure acid and water, formic acid is expected to form an aqueous negative binary homoazeotrope. Table 2 shows the close agreement between the experimental work of Roscoe and of Lecat on this homoazeotrope.

A weak acid whose boiling point is more than a few degrees above 100° C. cannot be expected to form an aqueous negative binary homoazeotrope because the concentration of ions produced cannot raise the boiling point of the solution above that of the pure acid, and so no maximum boiling point can be produced. Such is the case with acetic acid, $k = 1 \cdot 75 \times 10^{-5}$ at 25° C., b.p. = 118·1° C. This acid has been shown by Roscoe to form zeotropic aqueous solutions.

A weak acid whose boiling point is more than a few degrees below 100° C. cannot be expected to form an aqueous negative binary homoazeotrope because the depression of the boiling point of water by the presence of the more volatile undissociated molecules of acid will be greater than the elevation produced by the small concentration of ions. No aqueous negative binary homoazeotrope of a weak acid whose boiling point is lower than 99·9° C. has yet been encountered by the writer.

By similar reasoning weak bases whose boiling points are below that of water are expected to lower the boiling point of water. This has been shown

to be the case for n-butylamine, $k \doteq 10^{-4}$, b.p.$=77°$ C. The author wishes to thank Dr. Adrian Albert for supplying the n-butylamine with which the preliminary experiments have been performed; a full report of the results will, it is hoped, be submitted on a future occasion.

The Boiling Points of Aqueous Negative Binary Homoazeotropes.

Since a strong acid can provide a greater maximum concentration of ions than can a weaker, it is to be expected that the maximum boiling point of an aqueous solution of a strong acid will be higher than that of a weaker acid. But since an aqueous homoazeotrope of an acid contains some undissociated acid, this latter is one of the constituents of the mixture and therefore the boiling point of the mixture will be lower for a more volatile acid than for a less volatile acid of equal strength. These two effects are shown in Table 3. In this table the acids are divided into two groups, one contains those acids which when pure boil below 0° C., the other contains the less volatile acids. Each group is arranged in the order of descending boiling points of their aqueous homoazeotropes.

Table 3.

The Boiling Points of the Aqueous Homoazeotropes of Acids.

More Volatile Anhydrous Acids.	B.p. of the Azeotrope. ° C.	Less Volatile Anhydrous Acids.	B.p. of the Azeotrope ° C.
Hydriodic	127	Sulphuric	338
Hydrobromic	126	Perchloric	203
Hydrochloric	108·584	Nitric	120·5
		Hydrofluoric	120
		Formic	107

It will be seen that the acids in both groups fall into their generally accepted order of strength except in the case of sulphuric acid. It therefore appears that the boiling point of the aqueous negative homoazeotrope of a monobasic acid is a function of the strength of the acid and of the boiling point of the pure anhydrous acid:

$$T_c = f(k_a,\ T_o)$$

where T_c and T_o are the boiling points at 760 mm. of the acid-water homoazeotrope and of the anhydrous acid respectively, and k_a is a measure of the strength of the acid at the concentration of the homoazeotrope.

Summary.

It is suggested that the effect on the boiling point of water caused by the addition of a soluble electrolyte is determined by the presence of the ions produced and of any undissociated molecules. The ions raise the boiling point, while the molecules raise or lower it according to whether the boiling point of the pure electrolyte is above or below 100° C. As the concentration of an aqueous solution of a strong volatile acid is increased the boiling point will fall when the effect of the increasing quantity of undissociated molecules is greater than that of the ions. A weak electrolyte in aqueous solution is insufficiently dissociated to produce a detectable boiling point maximum unless the boiling point of the pure electrolyte is very close to 100° C.

The boiling point of an aqueous homoaezotrope of a monobasic acid appears to be an undetermined function of the boiling point of the pure acid and the strength of the acid at the concentration of its aqueous homoazeotrope.

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THE ELEMENTARY EXISTENCE THEOREM FOR DIFFERENTIAL EQUATIONS.

By W. B. Smith-White.

Communicated by Professor T. G. Room, F.R.S.

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The existence of solutions of a differential equation of the type

$$\frac{dy}{dx}=f(x, y_1), \qquad (1)$$

where $f(x, y)$ is continuous and satisfies the Lipschitz condition

$$|f(x, y_1)-f(x, y_2)|<K|y_1-y_2| \qquad (2)$$

near (x_0, y_0), is established by the method of successive approximations. There exists a unique solution

$$y=\varphi(x, c) \qquad (3)$$

defined near x_0 and having the value c for $x=x_0$, provided $|y_0-c|$ is sufficiently small. The function $\varphi(x, c)$ is continuous in both variables x and c near the point $x=x_0$, $c=y_0$. The general integral may be expressed in the form

$$\Omega(x, y)=c \qquad (4)$$

where c is an arbitrary constant, in the sense that this relation defines implicitly all the solutions of (1) in a restricted neighbourhood of (x_0, y_0).

For the general development of the theory of differential equations, and in particular for the study of more special problems connected with the solutions of (1) by the methods of the differential calculus, it is important to know whether the functions φ and Ω are differentiable with respect to their arguments. The condition (2) is not sufficient to establish this differentiability. The question is not adequately discussed in most text books ; for example the proof given by Bieberbach (1923) and by Ince (1927) that φ is differentiable with respect to c is not satisfactory.

We shall suppose that $f_y=\partial f/\partial y$ exists and is continuous ; this is a more restrictive condition than (2), and, as we shall see, implies the existence and continuity of the first derivatives of φ and Ω. For higher differentiability it would be necessary to assume the existence of higher derivatives of f. Differentiating (1) formally and writing $w=\partial y/\partial c=\partial\varphi/\partial c$ we have

$$\frac{dw}{dx}=wf_y(x, y) \qquad (5)$$

We may now consider (1) and (5) as a pair of simultaneous equations for the two functions y and w and apply the method of successive approximations to this system. In this way we may establish the existence of solutions

$$y=\varphi(x, c),\ w=\psi(x, c) \qquad (6)$$

reducing to $y=c$, $w=1$ when $x=x_0$.

However, the condition which corresponds to (2) for the case of two dependent variables is not satisfied by the pair of equations (1) and (5), and the

convergence of the successive approximations depends essentially on the special form of (5). Finally it may be shown that in fact φ is differentiable and

$$\frac{\partial\varphi}{\partial c}=\psi(x, c)$$

This method is explained in Goursat (1927).

The method given below is a little more direct and is more easily generalised to answer the corresponding questions for a system of simultaneous differential equations. Similarly we may discuss the question of the existence of higher derivatives. We use the following.

Lemma. Suppose $u(x)$ is continuous in $|x-x_0|\leqq h$, and that it has a derivative continuous in $|x-x_0|<h$. Write $u_0=u(x_0)$. If, for $K>0$ and $\delta\geqq 0$,

$$\left|\frac{du}{dx}\right|\leqq K|u|+\delta$$

then

$$|u|\leqq|u_0|e^{K|x-x_0|}+\frac{\delta}{K}(e^{K|x-x_0|}-1).$$

We prove this assuming $x_0=0$ and $0\leqq x\leqq h$. Then we have to show

$$|u|\leqq|u_0|e^{Kx}+\frac{\delta}{K}(e^{Kx}-1) \qquad \text{(7)}$$

Let $g(x)$ be a positive function such that

$$|u|\leqq|u_0|e^{Kx}+\frac{\delta}{K}(e^{Kx}-1)+g(x) \qquad \text{(8)}$$

Then

$$|u|=\left|u_0+\int_0^x\frac{du}{dx}dx\right|\leqq|u_0|+\int_0^x(K|u|+\delta)dx$$

$$\leqq|u_0|+\int_0^x\{K|u_0|e^{Kx}+\delta e^{Kx}+Kg(x)\}dx$$

$$\leqq|u_0|e^{Kx}+\frac{\delta}{K}(e^{Kx}-1)+K\int_0^x g(x)dx \qquad \text{(9)}$$

Clearly (8) holds with $g(x)=A$, a suitable positive constant; and then (9) shows that it holds also with $g(x)=AKx$. Applying the same transformation continually we see that (8) holds when $g(x)$ is any one of the functions

$$A,\ AKx,\ A\frac{(Kx)^2}{2!},\ldots,\ A\frac{(Kx)^n}{n!},\ldots$$

Hence

$$|u|\leqq|u_0|e^{Kx}+\frac{\delta}{K}(e^{Kx}-1)+A\frac{(Kx)^n}{n!}.$$

Letting $n\rightarrow\infty$, (7) is proved.

We wish to prove that the partial derivatives $\partial\varphi/\partial x$ and $\partial\varphi/\partial c$ exist and are themselves continuous in $|x-x_0|<h$, $|c-y_0|<k$, where h and k are suitably small. We have already

$$\frac{\partial\varphi}{\partial x}=f(x, \varphi(x, c))$$

and the right-hand side is a continuous function of both variables. Now, for $\Delta c\neq 0$, write

$$y=\varphi(x, c), \; y+\Delta y=\varphi(x, c+\Delta c)$$

so that $\Delta y\neq 0$ throughout $|x-x_0|\leqq h$ and $\Delta y=\Delta c$ if $x=x_0$. From (1)

$$\frac{d}{dx}\frac{\Delta y}{\Delta c}=\frac{\Delta y}{\Delta c}\frac{f(x, y+\Delta y)-f(x, y)}{\nabla y}=\frac{\Delta y}{\Delta c}\lambda \qquad (10)$$

where

$$\lambda=\lambda(x, \Delta c)=\frac{f(x, y+\Delta y)-f(x, y)}{\Delta y}.$$

By the mean value theorem

$$\lambda=f_y(x, y+\theta\Delta y)$$

where $0<\theta<1$; and since f_y is continuous near (x_0, y_0) we have $|\lambda|<K$ for some constant K. Further, as $\Delta c\to 0$, it follows from the continuity of $\varphi(x, c)$ that $\Delta y\to 0$ uniformly in $|x-x_0|\leqq h$, and then from the continuity of f_y that

$$\lambda\to\mu=\mu(x, c)=f_y(x, y) \qquad (11)$$

uniformly in $|x-x_0|\leqq h$. Let $w=\psi(x, c)$ be the solution of

$$\frac{dw}{dx}=w\mu \qquad (12)$$

which has the value 1 when $x=x_0$. If $u=\Delta y/\Delta c-\psi$, then $u_0=u(x_0)=0$ and from (10) and (12)

$$\frac{du}{dx}=u\lambda+\psi(\lambda-\mu) \qquad (13)$$

Given arbitrary $\varepsilon>0$, take δ so that $\frac{\delta}{K}(e^{Kh}-1)<\varepsilon$, and then, as ψ is bounded for given c, we may choose η so that, throughout $|x-x_0)\leqq h$ we have $|\psi(\lambda-\mu)|<\delta$ whenever $0<|\Delta c|<\eta$. From (13)

$$\left|\frac{du}{dx}\right|\leqq K|u|+\delta$$

and the lemma gives

$$\left|\frac{\Delta y}{\Delta c}-\psi\right|=|u|\leqq\frac{\delta}{K}(e^{K|x-x_0|}-1)\leqq\frac{\delta}{K}(e^{Kh}-1)\leqq\varepsilon$$

whenever $0<|\Delta c|<\eta$. We have thus proved that the limit

$$\frac{\partial\varphi}{\partial c}=\lim_{\Delta c\to 0}\frac{\Delta y}{\Delta c}$$

exists for each x in $|x-x_0|\leqq h$, and that it has the value $\psi(x, c)$.

Finally we show that $\psi(x, c)$ is a continuous function of both variables. From its definition (11) $\mu(x, c)$ is continuous, and so, for a suitable constant L, $|\mu(x, c)| < L$. Given arbitrary $\varepsilon > 0$, take δ so that $\frac{\delta}{L}(e^{Lh} - 1) < \varepsilon$. For a given value of c we may choose η so that

$$|\psi(x, c)(\mu(x, c') - \mu(x, c))| < \delta$$

whenever $|c' - c| < \eta$. If now $u = \psi(x, c') - \psi(x, c)$ we have $u_0 = u(x_0) = 0$, and from (12)

$$\frac{du}{dx} = u\mu(x, c') + \psi(x, c)(\mu(x, c') - \mu(x, c)).$$

Hence

$$\left|\frac{du}{dx}\right| < L|u| + \delta$$

The lemma gives

$$|\psi(x, c') - \psi(x, c)| = |u| \leqq \frac{\delta}{L}(e^{Lh} - 1) < \varepsilon$$

whenever $|c' - c| < \eta$. Hence $\psi(x, c)$ is continuous with respect to c, and this continuity is uniform with respect to x in $|x - x_0| \leqq h$. It follows that $\psi(x, c)$ is a continuous function of both variables x and c.

For $x = x_0$, $c = y_0$ we have $\partial\phi/\partial c = 1$. The relation (3) may therefore be expressed in the equivalent form (4), and $\Omega(x, y)$ will have continuous derivatives near (x_0, y_0); further $\partial\Omega/\partial y = 1$ for $x = x_0$, $y = y_0$.

Two well-known results which involve the existence theorems discussed above may be noticed. The first concerns a simple partial differential equation. Regarding x and c as independent variables, differentiate (4) with respect to x:

$$\frac{\partial\Omega}{\partial x} + \frac{\partial\Omega}{\partial y} \cdot \frac{\partial y}{\partial x} = 0;$$

hence

$$\frac{\partial\Omega}{\partial x} + \frac{\partial\Omega}{\partial y} f(x, y) = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

This is a partial differential equation; and we have established the existence of a solution of it $\Omega(x, y)$ having continuous derivatives provided the given function $f(x, y)$ and its derivative f_y are continuous.

Again, consider the expression

$$P(x, y)dx + Q(x, y)dy \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

where P and Q have continuous derivatives of the first order near (x_0, y_0). If $Q(x_0, y_0) \neq 0$ the equation

$$Q\frac{\partial\Omega}{\partial x} - P\frac{\partial\Omega}{\partial y} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

is equivalent to (14), and consequently has a solution $\Omega(x, y)$ for which $(\partial\Omega/\partial y)_0 \neq 0$.

Defining $M(x, y)$ by

$$\frac{\partial\Omega}{\partial y} = MQ$$

it follows from (16) that

$$\frac{\partial\Omega}{\partial x}=MP$$

and then

$$M(Pdx+Qdy)=d\Omega.$$

We have thus established the existence of an integrating factor $M(x, y)$ for the expression (15); this function $M(x, y)$ is continuous near (x_0, y_0) and $M(x_0, y_0)\neq 0$.

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SOME MINOR CONSTITUENTS OF EUCALYPTUS OILS.

Part I.

By C. Ralph, M.Sc.

Manuscript received, October 30, 1946. Read, December 4, 1946.

Considerable confusion exists amongst distillers of eucalyptus oils in the naming of their products, oil containing cineol being frequently described as that of *E. Australiana*, even when distilled from *E. dives* variety *C*. Care was taken, therefore, to check the sources of all the oils used in this investigation and to establish the identity of the various species from which they were distilled. The oils of *E. Australiana* examined were obtained from the Oberon and Tumut districts and that of *E. dives* variety *C*. from Tumbarumba.

Eucalyptus dives variety *C*.

Residues from the commercial distillation of this oil were found to contain much of the ester and free acid present in the crude material. The ester was isolated and shown to be methyl cinnamate, whilst the free acid present proved to be substantially pure geranic acid. A typical sample of crude commercial oil had an ester value of 14·9, corresponding to 4·4 per cent. methyl cinnamate, and an acid value of 2·1, equivalent to 0·7 per cent. geranic acid. The material remaining after the extraction of geranic acid from the highest boiling fractions crystallised on standing and was shown to be mainly eudesmol, identical with a sample isolated from the oil of *E. Macarthuri*.

Eucalyptus Australiana.

The still residue from this oil was also shown to contain methyl cinnamate (about 2% of the crude oil) and geranic acid (about 0·2% of the crude oil), though in this case some free cinnamic acid was also isolated. No tasmanol was detected in this oil (compare Baker and Smith, 1920). Various samples of the sesquiterpene alcohol present in *E. Australiana* oil were isolated, but these could not be induced to crystallise, and were not identified. A hydrocarbon with constants similar to those quoted by various authors for aromadendrene was also isolated from the oil.

Eucalyptus dives, type.

During the distillation of piperitone, separated from the oil of *Eucalyptus dives* by the bisulphite process, it was noticed that a crystalline material separated from the last fractions to distil over. Subsequent careful fractionation of the piperitone-free portion of the same oil gave a small fraction from which more of this material separated. Elementary analysis showed the compound to have the molecular formula $C_{10}H_{20}O_3$, and it was found to be saturated.

On acetylation a diacetate was formed, with elimination of water, from which the original compound could be recovered by alkaline hydrolysis. A further investigation of this unusual reaction is being carried out. The original material was very readily dehydrated by warming with dilute acid (0·4–15%

hydrochloric acid) to give p-cymene and l-carvotanacetone of high optical rotation ($[\alpha]_D$ $-58°\cdot5$).

Oxidation with alkaline permanganate gave a complex mixture of acids from which was isolated alpha-isopropyl-glutaric acid, showing that the compound must be *p-menthane-1 : 2 : 3-triol.*

An interesting aspect of the work carried out on the oils of *Eucalyptus dives* variety *C*. and *Eucalyptus Australiana* is the demonstration that these oils which contain the same principal constituents in approximately the same proportions are also alike in their minor constituents. Each oil contains 60–70% cineol, about 15% terpineol and a terpene fraction consisting principally of pinene together with methyl cinnamate and geranic acid and a sesquiterpene and sesquiterpene alcohol; the only differences noted were the failure to isolate crystalline eudesmol from *Eucalyptus Australiana* oil and the absence of free cinnamic acid in *Eucalyptus dives* variety *C*. oil. At the same time both *Eucalyptus Australiana* and *Eucalyptus dives* are known to exist in morphologically indistinguishable varieties which yield essential oils of thoroughly different types.

Experimental.

Eucalyptus dives variety C.

Still residues from about 1,700 kg. oil (55 kg.) were fractionated *in vacuo* to separate the terpineol (40 kg. crude) and higher fractions rich in ester and free acid. On refractionation of the latter portions the material boiling up to 128° C. at 10 mm. (300 ml.) was found to be rich in ester (ester value about 100) and by hydrolysis of a sample this was shown to be a cinnamate. The oil was repeatedly extracted with 80% v/v aqueous alcohol and the extract (230 ml.) was then boiled with 90% formic acid (180 g.) for ten minutes to dehydrate alcohols present. The crude ester was then separated by further extraction with 80% alcohol. Pure crystalline methyl cinnamate (30 g., b.p. 128–130° C. at 15 mm.) was obtained on distillation; no ester other than methyl cinnamate was detected in the oil examined.

The oil boiling from 128° to 152° C. (830 ml.) was viscous and contained free acid. It was dissolved in ether and the acid extracted with 6% aqueous sodium hydroxide. The residual oil was fractionated to give crystalline eudesmol (450 g., b.p. 145-150° C. at 8·5 mm.) which after recrystallisation from petroleum ether and finally from aqueous alcohol (Baker and Smith, 1920) melted at 79·5° C. and had $\alpha_D +37\cdot7°$. The melting point was undepressed by admixture with a sample of eudesmol prepared from the oil of *E. Macarthuri.*

The free acid (64 g.) was almost pure geranic acid (b.p. 138° C. at 10 mm.); it had $d_{25} 0\cdot951$, n1·4785. Found: C, 70·7%; H, 10·2%. Calculated for $C_{10}H_{16}O_2$: C, 71·5%; H, 9·5%. A sample of the acid was cyclised, with cold 60% sulphuric acid, to alpha-cyclogeranic acid (m.p. 104·5° C.). Found: C, 71·4%; H, 9·45%. Calculated for $C_{10}H_{16}O_2$: C, 71·5%; H, 9·5%. Cyclisation was also effected by refluxing for 80 minutes with 2·5 volumes of 90% formic acid.

Dihydroxy-dihydro-alpha-cyclogeranic acid was prepared by oxidation of alpha-cyclogeranic acid with permanganate. Found: C, 59·4%; H, 8·9%. Calculated for $C_{10}H_{18}O_4$: C, 59·4%; H, 8·9%. The pure product melted at 200° C. (decomp.). Identity of these acids was established by comparison with samples prepared from citral (Tiemann and Semmler, 1893).

Eucalyptus Australiana.

Distillation of 1,730 kg. oil (from Tumut) was carried out to give a B.P. distillate and 100 kg. residue; about 80 kg. crude terpineol (nitrosochloride, m.p. 122° C. undepressed by admixture with an authentic sample) was separated from this residue. Methyl cinnamate (140 g. crude crystals) was isolated by the method described above. The free acid in the oil of *Eucalyptus Australiana* was principally geranic acid, though free cinnamic acid was also isolated from the oil.

A sesquiterpene alcohol was isolated from this oil and this had properties similar to the corresponding fraction from *Eucalyptus dives* variety *C.* oil, but could not be induced to crystallise, despite repeated experiments with numerous samples from various localities.

During the fractionation of the residues from oil of *Eucalyptus Australiana*, a cut was made of material boiling from 100°–120° C. at 9 mm. This oil was insoluble in 70% v/v alcohol, but dissolved in 12 volumes 80% v/v alcohol. It contained much terpineol and methyl cinnamate. After repeated extraction of 560 g. with 80% v/v alcohol, an oil remained (87 g., $d_{23}0 \cdot 9200$ $\alpha D +22 \cdot 5°$) which was insoluble in this mixture. This material was repeatedly fractionated, first at atmospheric pressure, then over sodium, and finally under reduced pressure, to give a product (27 g.) boiling from 119–120° C. at 10 mm. It boiled at 264–267° C. at 760 mm. and had $d_{15}^{15}0 \cdot 9141$ $\alpha D +11 \cdot 9°$, n $1 \cdot 5010$, molecular refraction $65 \cdot 9$, constants similar to these quoted for aromadendrene (Baker and Smith, 1920; Briggs and Short, 1928).

The material, on dehydrogenation with selenium, gave a deep purplish-blue oil from which was prepared a black picrate, m.p. 116–118° C. Lack of material prevented further work being carried out.

Eucalyptus dives Type.

Isolation of p-menthane-1 : 2 : 3-triol. Crude piperitone (approx. 1,300 kg.) separated from *E. dives* oil by the bisulphite process, was distilled under vacuum (35 mm.) and the last 17 litres distilling over (b.p. approx. 150° C.) were set aside for some days. Colourless crystals separated out and were filtered and washed at the pump with alcohol. The yield varied from 20–200 g. This material readily recrystallised from alcohol to form large colourless crystals, m.p. 166° C. Found: C, $63 \cdot 6\%$; H, $10 \cdot 25\%$; molecular weight (by cryscopic determination in camphor), 177; calculated for $C_{10}H_{20}O_3$: C, $63 \cdot 8\%$; H, $10 \cdot 6\%$; m.w., 188.

A further yield of this material was obtained from the appropriate fraction distilled from the ketone-free material separated by sulphite.

Reactions of the Triol. p-Menthane-1 : 2 : 3-triol (15 g.) was refluxed with acetic anhydride (40 g.) and anhydrous sodium acetate (5 g.) for two hours and the product separated and distilled at 9 mm. pressure. Yield, 12 g.; b.p., 137–138° C. Found: C, $65 \cdot 9\%$; H, $8 \cdot 5\%$; ester value, 434. Calculated for $C_{10}H_{16}(OCOCH_3)_2$: C, $66 \cdot 1\%$; H, $8 \cdot 65\%$; ester value, 440.

The ester on hydrolysis with dilute aqueous-alcoholic potassium hydroxide gave the origina triol, m.p. 165° C.

The crystalline triol (65 g.) was refluxed for 90 minutes with a mixture of 10E hydrochloric acid (145 g.) and water (290 g.) and the resulting oil steam distilled from the mixture. Yield, 60 ml. This oil was shaken on the water bath with saturated sodium sulphite solution (800 ml.) containing phenolphthalein, the sodium hydroxide liberated being neutralised as it formed with 10% acetic acid. After two and a half hours, the unabsorbed oil (24 ml.) was separated, dried and fractionated, finally over metallic sodium. It boiled from 175–176° C. and had d_{22}^{22} $0 \cdot 8560$, n1 $\cdot 4950$ and was p-cymene. The sulphite solution was made strongly alkaline with potassium hydroxide solution and the liberated oil extracted with ether, dried with anhydrous sodium sulphate and distilled. Yield, 23 ml. The oil had b.p. 228° C. at 760 mm., d_{19}^{19} $0 \cdot 9323$, $[\alpha]D$ $-58 \cdot 5°$, and gave an oxime, m.p. 75–77° C., semicarbazone, m.p. 175° C., phenylhydrazone, m.p. 91–92° C., H_2S compound, m.p. 232–234° C., and dinitrophenylhydrazone, m.p. 193–193·5° C. These are the constants of carvotanacetone.

Carvotanacetone dinitrophenylhydrazone was prepared by adding carvotanacetone (1 g.) to a solution of dinitrophenylhydrazine (1·2 g.) in alcohol (5 ml.) containing a few drops of sulphuric acid. A red precipitate formed at once and was separated and recrystallised to constant melting point from acetone. Found: N, $16 \cdot 8\%$. Calculated for $C_{16}H_{20}N_4O_4$: N, $16 \cdot 85\%$.

Preparation of Alpha-isopropyl-glutaric Acid. The triol (30 g.) was finely powdered and added to a solution of sodium hydroxide (10 g.) in water (250 ml.) and oxidised by addition of cold 10% aqueous potassium permanganate solution, the reaction temperature being about 30° C. Just over a litre of permanganate solution was used. The crude mixture of acids was extracted from its solution, which had been concentrated after acidification to distil out volatile

acids (yield 15 g.) and warmed with an equal volume of aniline. After standing for some time the mixture set solid and was filtered and well washed at the pump with benzol and alcohol. Yield, 5 g. The aniline salt was recrystallised from its hot concentrated alcoholic solution, m.p. 153° C.

Found: Equivalent weight by titration, 179; N, 8·3%. Calculated for $C_8H_{14}O_4.(C_6H_5NH_2)_2$: E.W., 180; N, 7·8%. The free acid was separated from its aniline salt by extraction of an acidified aqueous solution of the salt with ether and recrystallisation from a mixture of chloroform and petroleum ether. M.p., 95–96° C.; equivalent weight (by silver salt), 88·5.

The aniline salt was obtained, though in smaller yield, by oxidation of pure piperitone, m.p. 153° C., undepressed by admixture with the corresponding salt from the triol. The acid must therefore be alpha-isopropyl-glutaric acid.

When separation of the aniline salt from the crude reaction mixture was found to be difficult, the acid mixture was esterified with alcoholic hydrochloric acid, the ester fraction boiling from 152–160° C. at 28 mm. separated and hydrolysed and the resultant acid treated with aniline. This procedure, however, was only occasionally found necessary.

Acknowledgments.

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THE CHEMISTRY OF RUTHENIUM.

PART I. THE REDOX POTENTIAL OF THE TRIS-ORTHOPHENANTHROLINE RUTHENOUS ION.

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and R. S. NYHOLM, M.Sc.

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The substance 2 : 2′ dipyridyl forms a remarkably stable series of red complex salts of bivalent ruthenium, which have been resolved into equally stable optical forms (Burstall, 1936). Recently, Steigman, Birnbaum and Edmonds (1942) investigated the possibilities of tris-dipyridyl ruthenous nitrate as an oxidation/reduction indicator and found that the reaction:

$$Ru(dipy)_3^{++} \text{ (red)} \rightarrow Ru(dipy)_3^{+++} \text{ (blue)} + e$$

involves a potential of $+1 \cdot 33$ volts. From experiments on the instability constants of the analogous ferrous tris-orthophenanthroline and tris-dipyridyl ions it was found that the orthophenanthroline complex was the more stable (Dwyer and Nyholm, 1946). Hence it is reasonable to conclude that the ruthenium orthophenanthroline complex would be more stable than the dipyridyl compound, and thus have an even higher redox potential.

The orthophenanthroline complexes, which have not been previously described, were prepared by treating a faintly acid solution of potassium pentachlorohydroxy ruthenate with orthophenanthroline ($3 \cdot 1$ mols.) and then heating for a short time with sodium hypophosphite, when a deep orange red solution of the tris-orthophenanthroline ruthenous chloride resulted. The substance could be isolated from solution as the sparingly soluble iodide, perchlorate, or thiocyanate. Other salts were then prepared from the free base $Ru(C_{12}H_8N_2)_3(OH)_2$, obtained by shaking the iodide with silver oxide.

As Burstall found with dipyridyl, these complexes of bivalent ruthenium are remarkably easy to prepare. Solutions of potassium hexachlororuthenate, pentachlorohydroxy ruthenate, or pentachloroaquo ruthenite in the presence of orthophenanthroline were slowly reduced by even hot alcohol to the ruthenium II compound. The complex chloride could be prepared in a similar manner to the dipyridyl compound by heating a mixture of potassium pentachloroaquo ruthenite with excess of orthophenanthroline at 250°, and although better yields, reckoned on the ruthenium used, were obtained, the method was wasteful of orthophenanthroline.

The free base was a strong alkali, which liberated ammonia from ammonium salts, and absorbed carbon dioxide from the air. The orange red salts were stable to boiling concentrated hydrochloric acid, and hot 5 N caustic soda. With concentrated nitric acid the substances became green due to partial oxidation to the ruthenium III compound. Acid permanganate and dichromate also partially oxidised them, but complete oxidation to the unstable blue ruthenium III compounds required the use of nitrato or sulphato ceric acid.

The redox potential of the system $Ru(phen)_3^{++} \rightarrow Ru(phen)_3^{+++} + e$ was determined in the usual way by potentiometric titration in solutions of varying

acid concentration using sulphato-ceric acid in the range 6 N to 12 N sulphuric acid, and nitrato-ceric acid in the lower acid concentrations. The titration method never gives accurate redox values owing to the establishment of false equilibria and the complexity of the solutions, but in this case it was not possible to measure the potential of equimolar mixtures of the pure oxidised and reduced forms owing to the instability of the oxidised form.

The potential was found to vary inversely as the acid concentration, so that below an acid concentration of 6 N a definite end point could not be obtained with sulphato-ceric acid, and the stronger oxidising agent nitrato-ceric acid had to be used. Unlike the corresponding system with ruthenous tris-dipyridyl, however, the system was unstable in all acid concentrations, and the blue oxidised form rapidly underwent self-reduction. This reaction was most pronounced in the lower acid concentrations where the potential was highest. As a result all titrations were necessarily performed as rapidly as possible without waiting for the system to come to equilibrium. All values obtained are consequently low, especially in the weakly acid solutions. The reduction of the blue oxidised form probably occurs by oxidisation of the orthophenanthroline ring to 3 : 3′-dicarboxy-2 : 2′-dipyridyl, which does not act as a chelate group due probably to steric interference of the carboxyl groups (Smirnoff, 1921). It is well known that orthophenanthroline is oxidised to the dicarboxylic acid by alkaline permanganate (Smith, 1924), and it was found that the potential of mixtures of nitrato-ceric acid and orthophenanthroline fell quite rapidly.

The potential in 1 N nitric acid was 1·29 volts as against 1·33 volts for the corresponding dipyridyl compound. This does not necessarily mean, however, that the stability of the orthophenanthroline ruthenium complex is lower than the dipyridyl complex, but probably that orthophenanthroline itself acts as a reducing agent at high potentials.

Experimental.

Tris-orthophenanthroline Ruthenous Perchlorate.

Potassium pentachlorohydroxy ruthenate (0·9 g.) was dissolved in hot water (50 mls.) containing one drop of hydrochloric acid (5 N.) and orthophenanthroline (1·65 g.), added with shaking. The mixture was boiled for a few minutes, when a deep greenish brown solution resulted. Hypophosphorous acid (30%, 2 mls.) neutralised with sufficient caustic soda (2 N.) was then added and the mixture refluxed for 10–15 minutes, when the colour had changed to deep orange red. The solution was filtered from traces of ruthenium metal, and perchloric acid (60%, 10 mls.), added drop by drop to the hot filtrate, with vigorous shaking to induce crystallisation. The substance after crystallisation from hot water in which it is only sparingly soluble gave purplish red square plates.

Found: C=49·2%; H=3·15%; N=9·63%. Calculated for $Ru(C_{12}H_8N_2)_3(ClO_4)_2.2H_2O$: C=49·2%; H=3·20%; N=9·58%.

Tris-orthophenanthroline Ruthenous Iodide.

This was prepared as above save that potassium iodide was substituted for perchloric acid. The substance was crystallised from water, in which it is somewhat more soluble than the perchlorate, and gave deep orange red cruciform prisms and rods.

Found: C=46·9%; H=2·86%; N=9·21%; I=27·4%.

Calculated for $Ru(C_{12}H_8N_2)_3.I_2.H_2O$: C=47·2%; H=2·86%; N=9·19%; I=27·79%.

Tris-orthophenanthroline Ruthenous Chloride.

The iodide in warm water was shaken with a large excess of silver oxide, and then filtered from excess of the oxide and the precipitated silver iodide. The resulting deep orange red solution of the free base on evaporation over solid caustic potash gave orange red hygroscopic plates of the hydroxide. This substance readily absorbed carbon dioxide, liberated ammonia

from ammonium salts, precipitated metallic hydroxides from solutions of their salts and was readily transformed into the chloride by treatment with hydrochloric acid. The substance crystallised from a little water gave dark red rhombs. It was easily soluble in cold water.

Found: $C=50\cdot39\%$; $H=4\cdot66\%$; $Cl=8\cdot13\%$. Calculated for $Ru(C_{12}H_8N_2)_3Cl_2.8H_2O$: $C=50\cdot41\%$; $H=4\cdot67\%$; $Cl=8\cdot28\%$.

Tris-orthophenanthroline Ruthenous Nitrate.

The free base was neutralised with nitric acid, and the solution evaporated over caustic potash. The bright orange red prisms and leaflects of the hexa hydrate were efflorescent. The substance was not as soluble as the chloride, and the solubility was lowered considerably by the presence of nitric acid.

Found: $C=54\cdot2\%$; $H=3\cdot37\%$. Calculated for $Ru(C_{12}H_8N_2)_3(NO_3)_2 1\cdot5H_2O$: $C=54\cdot47\%$; $H=3\cdot43\%$.

Tris-orthophenanthroline Ruthenous Bromide.

The free base was treated with hydrobromic acid or alternatively potassium bromide was added to solutions of the chloride or nitrate. The substance, which is a little more soluble than the iodide, was recrystallised from hot water, and gave orange red plates.

Found: $C=47\cdot26\%$; $H=3\cdot94\%$; $Br=17\cdot86\%$. Calculated for $Ru(C_{12}H_8N_2)_3Br_2.6H_2O$: $C=47\cdot53\%$; $H=3\cdot99\%$; $Br=17\cdot9\%$.

Tris-orthophenanthroline Ruthenous Tartrate.

The free base was treated with tartaric acid, or a saturated chloride solution was shaken with a large excess of ammonium tartrate. The impure crystals were dissolved in alcohol, the solution filtered, and either evaporated at room temperature or precipitated with ether. The substance was finally crystallised from a small volume of water. The orange red rhombs were very soluble in water. Attempts at resolution by the method employed by Burstall for the dipyridyl compound were unsuccessful.

Found: $C=51\cdot18\%$; $H=4\cdot06\%$; $N=8\cdot17\%$.

Calculated for $Ru(C_{12}H_8N_2)_3(C_4H_4O_6)_2.5H_2O$: $C=51\cdot3\%$; $H=4\cdot11\%$; $N=8\cdot17\%$.

Redox Potential Measurements.

The potentiometric titrations were carried out at 15° C. in a small five-neck flask, fitted with a stirrer, platinum electrode, salt bridge connected to a saturated calomel electrode, burette and carbon dioxide inlet tube. The potential was measured with a Leeds and Northrup type K potentiometer. For the first series of determinations the perchlorate, which can be obtained in a high state of purity, was used. The compound, $0\cdot1$ g., was dissolved in 50 mls. of the sulphuric acid at the particular concentration, and the oxygen removed from the solution by passage of carbon dioxide. With the stirrer in operation and the carbon dioxide passing the titration was carried out as rapidly as possible with $0\cdot05$ N sulphato-ceric acid. For the determinations in the lower acid concentrations, in order to give the solution sufficient "poise" the more soluble nitrate in $0\cdot002$ M. solution was titrated with $0\cdot05$ N nitrato-ceric acid. The end point was obtained in the usual way from the titration curve and the potential at the point of equivalent concentration of the oxidised and reduced forms obtained. The results are summarised in Table I and the effect of acid concentration on the potential is shown in Curve I.

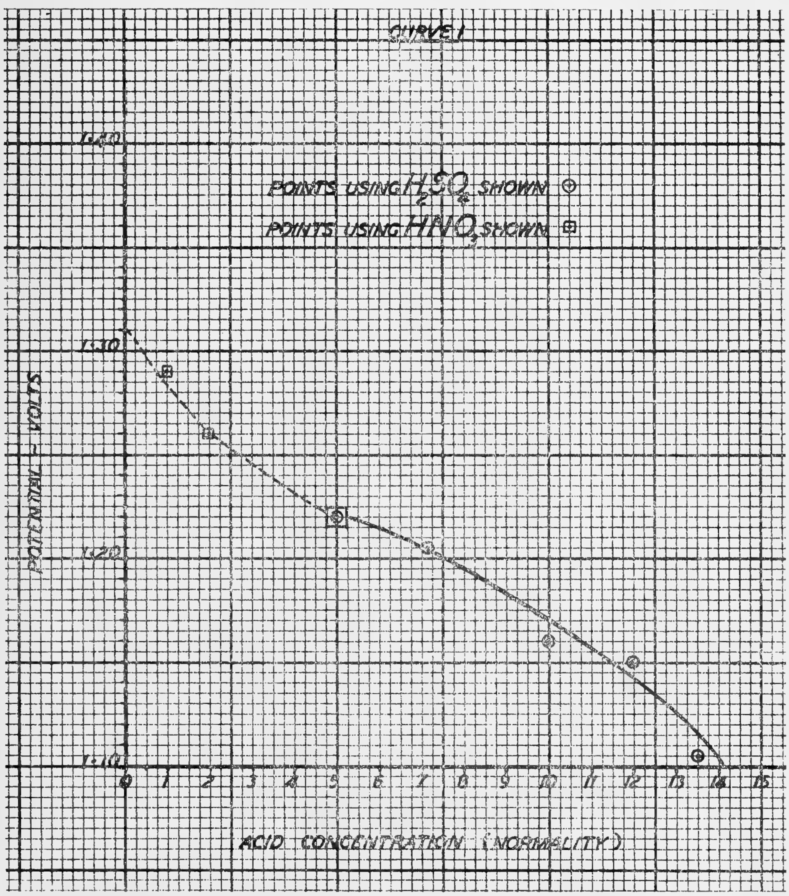
Summary.

A number of highly stable, orange red salts of the tris-orthophenanthroline ruthenous ion have been made from the chloride, which is obtained in excellent yield by reduction of mixtures of potassium pentachloro-hydroxy ruthenate and orthophenanthroline with hypophosphorous acid. The oxidation potential of the tris-orthophenanthroline ion in normal nitric acid was found to be $1\cdot29$ volts.

TABLE I.

The Oxidation Potential of Tris-orthophenanthroline Ruthenous Ion in Various Acid Concentrations.

Acid.	Concentration.	E.
Sulhpuric	13·5 N	1·105 volts
,, ...	12·0 N	1·15 ,,
,, ...	10·0 N	1·16 ,,
,, ...	7·1 N	1·205 ,,
,, ...	5·0 N	1·22 ,,
Nitric	5·0 N	1·22 ,,
,, ...	2·0 N	1·26 ,,
,, ...	1·0 N	1·29 ,,



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THE CHEMISTRY OF RUTHENIUM.

PART II. COMPLEXES OF DIPHENYL-METHYL-ARSINE WITH TRIVALENT AND DIVALENT RUTHENIUM HALIDES.

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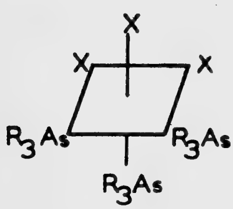
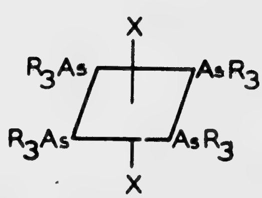
Recently it was shown that iron yields two types of complex with tertiary arsines—$2FeCl_3 . 3Ars$ and $FeCl_3 . 2Ars$—in which the usual coordination number of ferric iron is maintained by halogen bridges (Nyholm, 1944), but no complexes were formed with ferrous salts. The ruthenium complexes described in this paper have been studied as an extension of investigations on the compounds of the elements of group 8 (Dwyer and Nyholm, 1942, 1944), and also to determine whether the marked chemical similarity of iron and ruthenium is maintained in the compounds with tertiary arsines.

Quadrivalent ruthenium, whether in the form of chlorruthenate or pentachlorohydroxy ruthenate, failed to yield complexes, but instead the arsine reduced the metal to the trivalent state. Since the estimated redox potential of the quadrivalent/trivalent ruthenium couple is approximately 0·85 volt, and the arsines have pronounced reducing properties, this is not unexpected. Burrows and Parker (1934) were unable to isolate arsine compounds of quadrivalent platinum, and Mellor, Morris and Burrows (1938) found that when arsines were allowed to react with cupric chloride, either the cuprous compound or a binuclear cuprous/cupric complex was formed.



$(RuX_3 \cdot 3Ph_2AsMe)$.

I.



$(RuX_2 \cdot 4Ph_2AsMe)$.

II.

Trivalent ruthenium halides, however, gave only one kind of complex—$RuX_3 . 3Ars$—as deeply coloured solids, easily soluble in organic solvents. The halogen was not precipitated by cold alcoholic silver nitrate, and the compounds are ascribed the simple hexacovalent formula (I), analogous to the rhodium (III) and iridium (III) compounds. Efforts to prepare compounds of the type $RuX_3 . 2Ars$ and $2RuX_3 . 3Ars$ were unsuccessful, and it is concluded that ruthenium does not show the same tendency as iron to form bridged complexes.

The trivalent complexes were easily reduced with hypophosphorous acid to the pale yellow, ruthenium II compounds of the single type $RuX_2 . 4Ars$ (II).

No compound of the type $RuX_2 . 3Ars$, which would involve a halogen bridge, could be isolated, although the reduction was performed in some instances on pure specimens of the tris-arsine ruthenium III compound. These compounds are thus also analogous to the rhodium and iridium compounds with arsines. Diphenyl-methyl-arsine does not confer on the bivalent state of ruthenium the same stability as the chelate groups 2 : 2′ dipyridyl or orthophenanthroline, and the arsine complexes were powerful reducing agents. With cold alcoholic silver nitrate the halogen was not precipitated, but when heated a dark colloidal suspension of silver metal was formed along with the silver halide.

Experimental.

Tris-diphenylmethylarsine Ruthenium III Chloride.

Potassium-aquo-pentachloro ruthenate solution (10 mls.) containing 0·1 g. of ruthenium was treated with alcohol (40 mls.) and heated to boiling and diphenylmethylarsine (0·7 g., 3 mls.) in alcohol (20 mls.) added. On refluxing, the mixture became dark red, and part of the complex was deposited as an oil. The refluxing was continued for 10 minutes, and the whole cooled and shaken with a little petroleum ether. The resulting dark red powder melted at 138–140° C., was sparingly soluble in alcohol, but easily soluble in acetone, benzene or chloroform to deep red solutions. By varying the proportions of arsine and ruthenium, it was not possible to prepare the ruthenium analogue of the iron compounds.

The analysis of the compound by direct ignition followed by reduction of the ruthenium dioxide in hydrogen was not satisfactory owing to the difficulty of volatilisation of all of the arsenic. It was found, however, that the substance could be decomposed by concentrated sulphuric acid and potassium nitrate without loss of ruthenium as the tetroxide, provided that the potassium nitrate was not added until the halogen was completely removed. Most of the sulphuric acid was finally evaporated, and the ruthenium precipitated with hydrazine in alkaline solution. The halogen was estimated by the distillation method devised by the authors for the analysis of the rhodium arsine complexes.

Found: Ru=10·7%; Cl=11·2%. Calculated for $RuCl_3.3(C_6H_5)_2CH_3.As$: Ru=10·81%; Cl=11·33%.

Tris-diphenylmethylarsine Ruthenium III Bromide.

The chloro compound was prepared as above using sufficient alcohol to prevent precipitation of the substance as an oil, and concentrated hydrobromic acid (5 mls.) was then added. On heating for a few minutes the bromide was thrown out, as a dark blue microcrystalline precipitate. It melted at 135° and dissolved in benzene, or chloroform, to a violet solution.

Found: Br=22·1%. Calculated for $RuBr_3.3(C_6H_5)_2CH_3.As$: Br=22·36%.

Tris-diphenylmethylarsine Ruthenium III Iodide.

This was prepared in a similar manner to the bromide by the substitution of aqueous alcoholic potassium iodide for the hydrobromic acid. The dark brown microcrystalline powder melted at 130°, and dissolved easily in covalent solvents to a deep brown solution.

Found: I=31·6%. Calculated for $RuI_3.3(C_6H_5)_2CH_3.As$: I=31·4%.

Tetrakis-diphenylmethylarsine Ruthenium II Chloride.

The tris arsine Ru III compound above was prepared using sufficient alcohol to prevent precipitation of the substance as an oil, and 30% hypophosphorous acid (3 mls.) added. On refluxing the colour changed to light yellow, and the compound was precipitated in the presence of petroleum ether by the addition of water. Better yields were obtained by using four moles of arsine in the preparation of the original Ru III compound. The substance was obtained as a yellow microcrystalline powder, easily soluble in alcohol, acetone and benzene, m.p. 155°. The

compound reduced hot alcoholic silver nitrate to the metal, and reacted with orthophenanthroline to give the orange yellow tris-orthophenanthroline Ru II complex.

Found: Ru=8·9%; Cl=6·3%. Calculated for $RuCl_2 4C_6H_5)_2CH_3.As$: Ru=8·86%: Cl=6·18%.

Tetrakis-diphenylmethylarsine Ruthenium II Bromide.

Prepared in a similar manner to the chloride above by the reduction of the Ru III compound, the yellow powder melted at 190°.

Found: Br=13·1%. Calculated for $RuBr_2.4(C_6H_5)_2CH_3.As$: Br=12·93%.

Tetrakis-diphenylmethylarsine Ruthenium II Iodide.

Reduction of the tris iodo Ru III compound gave a yellow microcrystalline substance, m.p. 155°.

Found: I=19·04%. Calculated for $RuI_2.4(C_6H_5)_2CH_3.As$: I=19·06%.

Summary.

Unlike iron, ruthenium III halides form only simple unbridged complexes with diphenylmethylarsine, of the type RuX_3 . 3Ars. Reduction with hypophosphorous acid leads to the ruthenium II complexes of the single type RuX_2 . 4Ars, in which the hexacovalency of the metal is also maintained without recourse to halogen bridges.

Acknowledgment.

The authors are indebted to the Commonwealth Research Committee for a grant for the purchase of ruthenium.

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Nyholm, 1944. This Journal, **78**, 229.

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T—December 4, 1946.

PYRIDINE CO-ORDINATED IODINE SALTS OF DIAZOAMINO COMPOUNDS.

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When the cupric salts of many diazoamino compounds are boiled with alcohol disproportionation occurs, and the cuprous salt results (Dwyer, 1939). In an effort to trace the cast off triazene radicle the reaction between iodine and the silver salts of diazoamino compounds has been studied. This reaction was expected to follow the course $2R_2N_3 . Ag + I_2 \rightarrow 2AgI + 2R_2N_3$.

In benzene or ether solution, however, iodine did not react with the silver salts of the triazenes, but in pyridine solution in every case, silver iodide was precipitated and a new type of iodine triazene complex formed.

With the silver salt of 3 : 4′-dinitrodiazoaminobenzene, upon which most of the tests were carried out, the deep red colour of the pyridine solution was discharged, silver iodide precipitated, and the yellow pyridine solution on dilution with water deposited yellow needles of a substance of the formula $(NO_2C_6H_4)_2N_3I . C_5H_5N$. This was insoluble in ether, benzene, or chloroform, but soluble in alcohol or acetone. It melted with decomposition liberating pyridine and violet vapours of iodine, and in warm alcoholic solution the free triazene was regenerated with the liberation of the iodine either as the element itself or as iodic acid. In hot acetone part of the iodine was transformed to iodoacetone. At room temperature it was reduced to the triazene by treatment with sulphurous acid, sodium thiosulphate and other reducing agents.

Since 3 : 4′-dinitrodiazoaminobenzene is unsymmetrical, it appeared likely that the position of the iodine atom could be located by methylation. On treatment with methyl magnesium iodide in ethereal suspension, however, a blue precipitate was formed, which was identical with that obtained from the original triazene, and on hydrolysis with water gave only 3 : 4′-dinitrodiazoaminobenzene and no trace of the N-methyl compound. The blue precipitate was thus the magnesium salt of the triazene and the reaction apparently followed the course

$$2R_2N_3I . C_5H_5N + 2CH_3MgI \rightarrow (R_2N_3)_2Mg + MgI_2 + 2CH_3I + 2C_5H_5N.$$

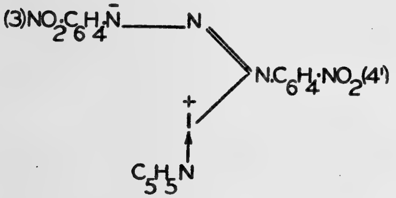
Similarly, when the substance was treated with zinc dust or sodium and methyl iodide either the yellow zinc salt or the dark red sodium salt of the triazene was formed. This evidence suggested that the compound did not contain the usual covalently bonded iodine, but was a pyridine co-ordinated iodine salt. The probable mode of formation from the well-known pyridine iodine compound $PyI^+ . I'$ (Feigl, 1940):

$$R_2N_3Ag + PyI^+ . I' \rightarrow PyI^+ . N_3R_2 + AgI$$

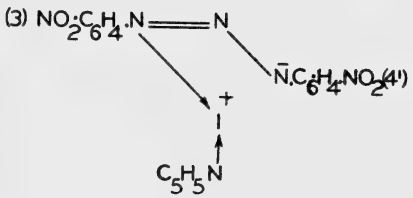
is in accord with this view, as is also the failure of the preparative reaction when solutions of iodine in benzene or ether, in which the halogen is present in molecular solution, are added to the triazene silver salt. Further evidence is afforded by the liberation of nitrogen gas when treated with aqueous alcoholic hydrazine (Macbeth, Nunan and Traill, 1926), and by the pronounced oxidising properties

of the substance. When shaken with aqueous alcoholic solutions of potassium iodide, bromide, chloride and nitrate, the dark coloured potassium salt of the triazene and the free halogen were formed with the first two substances, but no change occurred with the latter two. The reactions $2I' - 2e \rightarrow I_2$; $2Br' - 2e \rightarrow Br_2$ and $2Cl' - 2e \rightarrow Cl_2$ have potentials of 0·534, 1·065 and 1·358 volts respectively (Latimer, 1938), hence the iodine atom in the complex must be in a higher oxidation state than free iodine itself and have an oxidation potential between bromine and chlorine—approximately 1·2 volts.

The compound is accordingly formulated as a two-covalent iodine salt analogous to bis-pyridine iodine nitrate described by Carlson (1932). The existence of resonance forms (I) (I*a*) would account for the stability of the structure, as well as the failure to isolate two forms with unsymmetrical triazenes such as 3 : 4′-dinitrodiazoaminobenzene.



(I)



(Ia)

Although the silver salts of diazoaminobenzene itself and all of its mono and dinitro substituted derivatives reacted with iodine in pyridine solution with precipitation of silver iodide, the iodo complexes of 3 : 3′, 3 : 4′ and 4 : 4′ dinitro compounds only, could be isolated as pure substances. The other compounds either decomposed to the free triazene and hypoiodous acid on the addition of water to the pyridine solution or during crystallisation from alcohol or acetone whilst seeking to remove traces of silver iodide.

The low stability of the iodine complexes from diazoaminobenzene itself and the mono-nitro compounds is understandable in view of the lower acidity of the parent triazenes, but the failure to isolate the pure complex of any dinitro compound with an ortho nitro group is unexpected since all of the dinitro triazenes are more acidic than the 3 : 3′ dinitro compound. A possible reason is steric hindrance, and in this regard the observation of Meldola and Streitfeild (1896) that 2 : 2′-dinitrodiazoaminobenzene can be methylated but not ethylated, whilst N-ethyl-2 : 4′-dinitrodiazoaminobenzene has the ethyl group on the triazene nitrogen remote from the ortho nitro group, is significant.

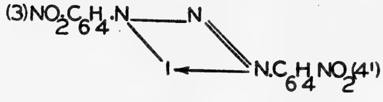
The pyridine could be removed from the compounds with dilute acids, but unless the pyridine-free compound was removed from contact with the acid as fast as it was formed it decomposed to the triazene and the iodine salt of the acid.

$$R_2N_3I.C_5H_5N + 2HNO_3 + (C_2H_5OH) \rightarrow R_2N_3H + INO_3 + C_5H_5NHNO_3 + (C_2H_5OH).$$

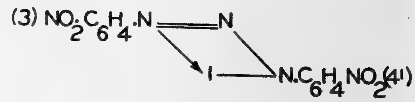
However, when suspended in ether and shaken with the exact amount of dilute acid, the substances lost pyridine and passed into solution in the ether. Evaporation then gave the pyridine-free complexes as yellow unstable needles, which spontaneously evolved iodine, probably by reaction with traces of water. Small amounts of the free triazene were always present, and all attempts at purification led to complete decomposition. They were very soluble in ether, benzene, petroleum ether and chloroform, and are probably covalent iodine compounds. The existence of resonating forms (II) (II*a*) is probable.

The compound N-iodo-3 : 3′-dinitrodiazoaminobenzene was the most stable, then the 3 : 4′-dinitro compound, whilst traces only of the 4 : 4′-dinitro compound could be isolated. Nitro group substituents in diazoamino compounds

have a similar effect as with the phenols, and all nitro derivatives are stronger acids than diazoaminobenzene itself, whilst with *o* or *p* nitro groups enhanced acidity results from resonance.

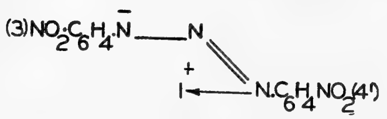


(II)

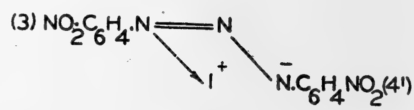


(IIa)

In structures of the type (II) (II*a*) the stability might be expected to be associated chiefly with the donor properties of the triazene nitrogens, and hence the nitro groups should lower the stability in the order meta, ortho, para, as found. But in this case the iodo compound of diazoaminobenzene itself should be the most stable of all, whereas, actually no trace of a compound can be isolated. This suggests that resonant ionic forms (III) (III*a*) must also contribute to the stability of the structure.



(III)



(IIIa)

Experimental.

Mono-pyridine-N-iodo-3 : 4′-dinitrodiazoaminobenzene.

The silver salt of the triazene (2 g., 1 mol.) and pyridine (100 mls.) were stirred at room temperature, and iodine (1·27 g., 1 mol.) added gradually. The deep red solution lightened, and silver iodide precipitated together with some of the iodo compound. Stirring was continued until the colour had changed to yellow, and water added. The solid was collected, extracted with acetone to remove the iodo compound, which was finally precipitated with water. The substance crystallised from pyridine in bright yellow needles, which darkened on exposure to light, and melted at 123° with decomposition. It was easily soluble in nitrobenzene, and cryoscopic determination of the molecular weight in this solvent showed it to be dissociated. The determination of the molecular weight was difficult owing to the pronounced tendency of the solution to supercool.

Found: I=25·8%; N=16·95%. Mol. wt.: 245. Calculated for $(C_6H_4NO_2)_2N_3I.C_5H_5N$: I=25·85%; N=17·08%. Mol. wt., 492.

Mono-pyridine-N-iodo-3 : 3′-dinitrodiazoaminobenzene.

Prepared as above, the pale yellow needles from acetone melted at 112·5° (decomp.).

Found: I=25·0%; N=17·02%. Calculated for $(C_6H_4NO_2)_2N_3I.C_5H_5N$: I=25·8%; N=17·08%.

Mono-pyridine-N-iodo-4 : 4′-dinitrodiazoaminobenzene.

The fine reddish needles from acetone or pyridine melted 136–137° (decomp.).

Found: I=25·0%; N=16·96%. Calculated for $(C_6H_4NO_2)_2N_3I.C_5H_5N$: I=25·8% l N=17·08%.

Attempts to Prepare other Iodo Complexes.

When the silver salts of 2 : 4′ and 2 : 3′ dinitrodiazoaminobenzene in pyridine solution were treated with iodine, the usual precipitation of silver iodide occurred, and addition of water

then gave a precipitate of the iodo complex mixed with some free triazene and silver iodide. Extraction with cold acetone dissolved the iodo compound and the triazene, but the yellow crystalline product obtained by the careful addition of water melted over a range of several degrees. Further crystallisation from acetone caused a loss of iodine and the melting point approached that of the pure triazene. The very stable red salt of 2 : 2′-dinitrodiazoaminobenzene also reacted with iodine, but the iodo compound was completely decomposed on the addition of water to the pyridine solution, and the pure diazoamino compound was recovered.

The most stable of the mono-nitro compounds—mono-pyridine-N-iodo-4-nitrodiazoamino-benzene—was obtained as a reddish oil by the addition of dry iodine to the dry silver salt in dry pyridine, filtering off the silver iodide, and precipitating with petroleum ether. The oil solidified on trituration with petroleum ether to a brownish yellow powder, which, however, contained a little silver iodide. The substance decomposed when crystallised from acetone, whilst crystallisation from pyridine and petroleum ether failed to remove the silver iodide. The impure compound melted at 77–79°.

Found: $N=14 \cdot 47\%$. Calculated for $C_{17}H_{13}O_2N_5I$: $N=15 \cdot 67\%$.

The iodine split off by the decomposition of the above compounds in aqueous pyridine or acetone was precipitated with the free triazene as pyridinium iodate. Treatment with dilute acid gave a solution of iodic acid, which then liberated iodine when potassium iodide was added.

Summary.

The silver salts of 3 : 3′, 3 : 4′ and 4 : 4′-dinitrodiazoaminobenzene reacted with iodine in pyridine solution with the formation of silver iodide and mono-pyridine-N-iodo diazoamino compounds as yellow crystalline substances. In these compounds it is considered that the iodine functions as a two-covalent cation. Highly unstable ring compounds of iodine arise by the removal of the pyridine with dilute acid in the presence of ether.

Acknowledgments.

The authors are indebted to Mr. G. K. Hughes for many helpful comments, and to Miss Fildes for nitrogen analyses.

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A NOTE ON THE ESTIMATION OF SOME AROMATIC HYDROXY-COMPOUNDS.

By J. A. Friend, B.Sc.

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The object of this note is to describe the use of Millon's reagent, as modified by Folin and Ciocalteu (1927), for the estimation of esters of *p*-hydroxybenzoic acid by a colorimetric method. Preliminary tests of the phenol reagent of Folin and Looney (1922) showed that it was unsatisfactory for this purpose. The original Millon's reagent has been used previously for the estimation of *p*-hydroxybenzoic acid (Edwards *et al.*, 1937), but the reagent used in the present work has the advantage of being stable, which the original reagent is not. There seems to be no great difference in sensitivity between the two reagents.

Experimental.

Tests were carried out with a millimolar solution of the methyl *p*-hydroxybenzoate to see if the colour was satisfactory for quantitative work. The tests took the following form :

5 ml. of the test solution was heated on the water bath with 5 ml. of $HgSO_4$ solution (15 g. $HgSO_4$ in 100 ml. $6N.H_2SO_4$). After 15 minutes, the solution was cooled and 1 ml. of $NaNO_2$ (2 g. in 100 ml. H_2O) was added. A bright cherry red colour was developed, and found to be fully reproducible at a given concentration. Furthermore, over quite a considerable range of concentrations the colour intensity was proportional to the concentration of the ester present, as is shown in the following table. "Colorimeter reading" refers to readings on the scale of a Klett colorimeter, and the figures quoted are the mean in each case of six readings. It will be seen that the product (concentration × reading) is almost constant.

Table I.

Concentration (c) of Methyl *p*-OH-benzoate.	Colorimeter Reading (r).	$c \times r$.
mM.		
5	8·0	40·0
4	10·2	40·8
3	13·3	39·9
2	20·3	40·6
1	40·2	40·2

Normally, of course, better results are obtained if the concentrations studied cover a range of 0·5–1·5 times that of the standard. However, in this work it was more convenient to use a concentrated standard and have the unknown solutions of lower concentration. In favourable cases, a concentration one-tenth that of the standard could be read off with an accuracy of about ±2%.

Having thus established the general usefulness of the modified Millon reagent for the methyl *p*-hydroxybenzoate, the ethyl, propyl, butyl, amyl, hexyl and heptyl esters were next examined. On doing this, two conclusions were reached. The first was that for a given concentration of the

parent acid and the esters from methyl to butyl, the colour developed was constant in intensity. This is contrary to the finding of Edwards *et al.* (*loc. cit.*). For esters above butyl, two difficulties arose : the solutions obtainable were too dilute for a useful comparison to be made, and the colour developed differed from that of the standard. It was found convenient to use a 1 mM. solution of the methyl ester as a common standard when a mixed batch comprising all these esters was to be examined. Table 2 shows the colorimeter readings for 1 mM. solutions of various esters ; they are constant within a range of $\pm 5\%$.

TABLE II.

Solution.	Colorimeter Reading.
1 mM methyl ester	10·0 (standard)
,, ,, ethyl ,,	10·0, 10·1, 10·0
,, ,, propyl ,,	10·2, 10·3, 10·2
,, ,, butyl ,,	10·4, 10·4, 10·8

The second difficulty mentioned constitutes a limitation to the usefulness of the method, particularly in very low concentrations. The colour variation was nearly always towards the yellow, but on one occasion a saturated (*ca.* 0·3 mM.) solution of the amyl ester gave a bluer shade than the standard, and on filtration a bluish-red substance could be isolated from the solution. It was later found that a solution of the free acid (7·25 mM.) gave such a precipitate on standing after colour-formation.

From Fig. 1 it will be seen that the absorption spectrum of the coloured solution underwent a substantial change when a precipitate formed, chiefly in the sharpness of the absorption. The

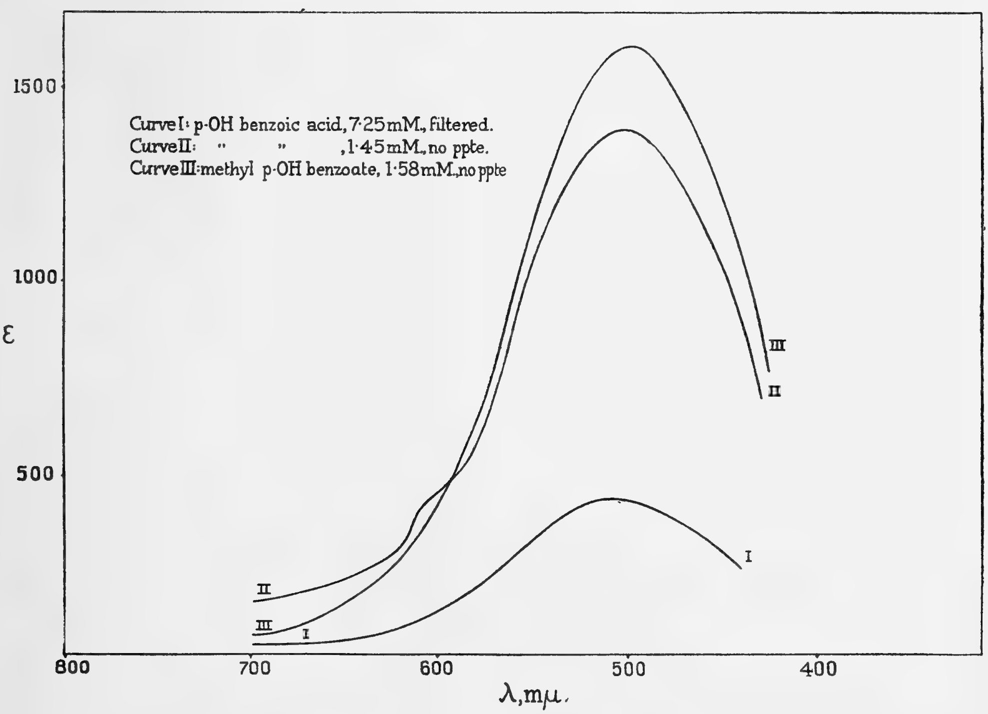

Fig. 1.

figure also shows that the absorption spectrum of the acid is different from that of the methyl ester, although the maximum absorption occurs at approximately the same wave-length. Obviously, for the weaker solutions a photo-electric colorimeter using a filter with maximum transmission at 480–550 mμ would give better results. Better still, a spectrophotometer could be used, and readings taken at 510 mμ, the region of the absorption maximum.*

Summary.

A method for the visual colorimetric estimation of derivatives of *p*-hydroxybenzoic acid, using Folin and Ciocalteu's $HgSO_4$-$NaNO_2$ reagent, is described. The method was found satisfactory (within $\pm 1\%$) over a range of concentrations from 0·1 to 5 mM. Amyl acetate occasionally interfered, possibly due to a mercurating action on the esters.

Acknowledgments.

The author is indebted to Mr. J. M. Vincent, Dr. D. P. Mellor and Mr. G. W. K. Cavill for advice and assistance in connection with this investigation.

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* One or two observations of interest may be mentioned. This work was done during an investigation of partition coefficients between water and amyl acetate. Under these conditions, it was necessary to use water saturated with amyl acetate, and occasionally a cream or white precipitate appeared during the heating of the solution. Following this, little or no colour was formed on adding sodium nitrite, showing that the precipitate contained mercury or the ester or both. Its nature was not fully investigated, but on ignition charring took place, indicating the presence of organic matter. Further, the compound could be reduced to mercury by boiling with ethanolamine, following Rauscher (1938). Thus, the organo-metallic nature of the precipitate was established. In passing, it might be mentioned that C-mercurial derivatives of *p*-hydroxybenzoic acid have been prepared (Whitmore, 1921).

Attempts were made, unsuccessfully, to find the cause of the appearance of the precipitate. It seems that the use of duplicate or triplicate estimations would avoid any trouble, as precipitation occurred only rarely.

SPECTROGRAPHIC ANALYSIS OF STEEL.

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With Plate VIII.

Manuscript received, November 20, 1946. Read, December 4, 1946.

Attempts to prepare " working curves " for Open Hearth Steels by the standard 15,000 volt condensed spark technique met with little success until the spectrograph and its adjustment, the plate processing and the adjustment of the microphotometer were investigated at some length. The details of these adjustments comprise the first two sections of this paper ; the final section deals with " arcing to completion ", a method for which some workers have claimed high accuracy. (Hasler and Harvey, 1943.)

Adjustment of the Spectrograph.

Slit Width.

Intensity Distribution.

When light is passed through a narrow slit, such as that of a spectrograph, diffraction takes place and instead of a geometrical image a system of diffraction bands is formed. The intensity at any point in the diffraction pattern is given by (Preston)

$$I=\int_{d-s/2}^{d+s/2}\frac{\sin^2 x\ dx}{x^2}$$

where s is the width of the geometrical image of the slit and d the distance of the point from the centre of the pattern ; $2x$ is the phase difference of the extreme rays at the point ; the amplitude of the vibration is assumed to be unity. The integral can be evaluated in the form of a series.

Values of the integral for a series of values of x were assembled in a table from which the values of $d+s/2$ and $d-s/2$ were extracted by addition and subtraction. Results for slit widths 0·005 mm., 0·025 mm. and 0·05 mm. are exhibited in the form of graphs in Figure 1. The scale of intensity is arbitrary in the graph and distances d from the centre were actually calculated in radians. It is seen that as the slit is widened the curve becomes flat topped—the half-value width (Baker, 1934) being approximately proportional to the slit width. Also, the intensity does not reach zero at any point in the diffraction pattern of slits of finite width. A flat-topped spectrum line would be an advantage in photometry but widths used in practice are usually less than 0·025 mm.

The peak intensity of the central maximum of the diffraction pattern for a series of slit widths is given in Table 1, in which an infinitely wide slit is taken as 100% intensity. This table was prepared in the hope of using slit width variation and line intensity as a method of plate calibration. However, with wide slits the background is very intense and with narrow slits it is too difficult to make accurate settings ; moreover diffraction widens the beam on the collimator

make accurate settings; moreover diffraction widens the beam on a collimator lens so that all light passing through the slit does not reach the plate. Table 1 shows that the rate of increase of intensity with increase of slit width diminishes as wider slits are approached.

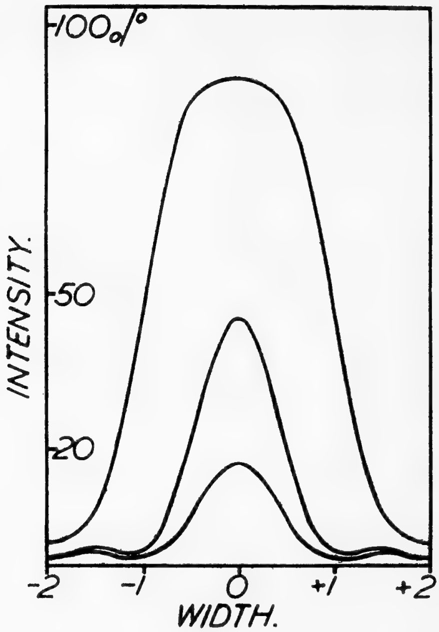

Figure 1.—Intensity distribution in the central maximum of the diffraction bands of slits 0.005, 0.025 and 0.05 mms.

TABLE 1.

Slit Width. mm.	Intensity. %
0·04	9
·09	25
·18	47
·29	68
·36	77
·50	88
·65	90
1·09	93
Infinite	100

Optimum Width.

Some writers do not agree entirely with the above calculations (van Cittert, 1930, 1931), but there is general agreement that the optimum width of slit is given by

$$s = \frac{f\lambda}{D}$$

where f is the focal length and D the diameter of the collimator lens and λ the wavelength of the light. This slit width is such that the half-value width of the

central maximum of the diffraction system is equal to the diameter of the collimator lens. In the case of the Hilger large quartz spectrograph s is approximately $0 \cdot 009$ mm. for 3,000 A. and the slit can be set at this width if the zero reading of the slit micrometer be known.

An approximate setting can also be made experimentally by placing a narrow source of light on the optical axis of the spectrograph at a distance of about a metre from the slit ; on looking into the camera an image of the source will be seen in the camera lens. As the slit is narrowed, secondary images appear on both sides of the main image and the latter widens ; when the central image covers the camera lens and no secondary images are visible the slit is at the optimum width for that wavelength. By employing a condensed spark discharge between 10 s.w.g. steel electrodes a setting of $0 \cdot 02$ mm. was obtained in the orange (about 6,000 A.) so that $0 \cdot 01$ mm. would be required for 3,000 A.—a result that agrees closely with the calculated value. Setting the slit experimentally led to the discovery of a zero reading of $-0 \cdot 02$ mm. on the slit micrometer in the present case.

Background.

The background of a line spectrum is continuous and as such its intensity is directly proportional to the slit width over wide limits. (Ornstein, 1935.)

Application to Spectrographic Analysis.

Let the intensity of an iron line be I_0 and let the background intensity on which the line is superposed be i_0. Let the corresponding intensities for an analysis line be I and i respectively. Then the ratio of the observed intensities is given by

$$R=\frac{I+i}{I_0+i_0}=\frac{I}{I_0+i_0}+\frac{i}{I_0+i_0}$$

$$=\frac{kc}{I_0+i_0}+\frac{i}{I_0+i_0}$$

where c is the concentration of the element for which analysis is made and it is assumed that $I=kc$, k being a constant.

Suppose the slit is at the optimum width or somewhat wider so that the intensity of the iron line is approximately independent of the slit width and we may put $\frac{k}{I_0+i_0}=l$. Also the second term depends only on the slit width and it may be denoted by S. Then

$$R=lc+S \text{ and } dR=ldc.$$

So that

$$\frac{dc}{c}=\frac{dR}{R}\times\frac{R}{R-S}.$$

If S be increased the right-hand side of this expression is increased, whereas if S were zero we would have $dc/c=dR/R$. Thus error in R causes least error in c when S is zero. Now S is diminished by narrowing the slit. Therefore since the concentration c of the element is determined by measuring R it is evident that the accuracy of spectrographic analysis is increased by reducing the slit width as much as practicable.

Focus.

With the slit at the optimum width and employing a fine grain emulsion such as the Kodak Process a series of photographs of an iron arc is taken with the focus set at different values on each side of the maker's value. When the

plate is processed, the photograph in which the lines are sharpest is selected with the aid of a magnifying glass.

An overall test of the optical components of the spectrograph and at the same time a more refined adjustment of the focus can be obtained by the Hartmann Test (Hartmann, 1900). A wide slit about ten times the optimum width and a narrow source are employed. A soft plate such as Kodak Orthochromatic is preferable here because it records the less intense scattered light.

Photometry.

The Microphotometer.

In view of the development of photoelectric devices that eliminate the photographic plate from the spectrograph (Saunderson, Caldecourt and Petersen, 1945) and hence render the microphotometer obsolete it was considered inexpedient to purchase a microphotometer. A satisfactory instrument was constructed on a small lathe bed with apparatus available in the laboratory (Baker, 1947).

Plate Processing.

Good results were obtained by treating Kodak Process Plates as follows: *Develop* in Kodak Developer D19 diluted 1 to 3 with water for 3 minutes at 20° C. ±0·5° C. Brush gently with a 3 in. varnish brush throughout development. *Fix* in Kodak X-ray Fixing Compound for 2 minutes at approximately 20° C. *Wash* in running water for 15 minutes and then place in distilled water to which a drop of Kodak Photoflow has been added for 2 minutes. *Dry* slowly in a rack if time permits.

At first a different method of processing was employed and the large variable errors encountered were thought to be due to the microphotometer. Some errors were due to scattered light and these were eliminated by blackening the inside of the tubes holding the lenses; it was also found that the microphotometer takes about half an hour to reach equilibrium after placing the galvanometer on suspension and energising the lamp. Further errors were due to the method of plate processing. The methods investigated were (*a*) moving stainless steel roller to and fro across the plate during development; the roller cleared the film by about $\frac{1}{32}$ in.; (*b*) dish rocking; lifting each side of the dish about 1 in. in turn about every second; holding the plate at the centre of the dish with glass strips; (*c*) brushing as set out above.

A quartz mercury vapour lamp operating at atmospheric pressure and energised by a 100 volt battery was placed on the optical axis of the spectrograph and run for half an hour so as to reach equilibrium. On each of nine plates ten spectrograms were then taken. The first, fourth and seventh plates were then processed with the roller, the second, fifth and eighth by dish rocking, and the third, sixth and ninth by brushing. Assuming that the mercury lamp intensity is constant, measurements of these nine plates indicated that the microphotometer is capable of detecting a density variation of 0·01 for densities between 0·8 and 1·6. Variation in the density of a spectrum line across three plates, i.e. for 30 galvanometer readings, was not more than 0·07 for the roller, 0·05 for dish rocking, and 0·03 for brushing. Further investigation of dish rocking suggests that the quantity of developer may be at least halved, because apparently exposure of the film to air during the rocking process does not affect the uniformity of development; a mechanical rocker might make this equal to the brushing method.

Plate Calibration.

The plate was calibrated by setting a high-pressure quartz mercury vapour lamp about a metre in front of the spectrograph slit and taking a series of

exposures with the slit width at 1, 2, 4, 8, 16, 32 and 64 scale divisions, the exposure being the same in each case. The slit widths employed are wide enough to avoid loss of light by diffraction at the slit. A 150-watt mercury street lamp with a hole cut in the outer glass envelope and run from the A.C. supply was satisfactory. Microphotometer readings of the background at the appropriate wavelength are then plotted against slit width on log-linear paper. A typical plate characteristic curve is shown in Figure 2, in which the left-hand ordinate represents the usual linear galvanometer scale and the right-hand ordinate

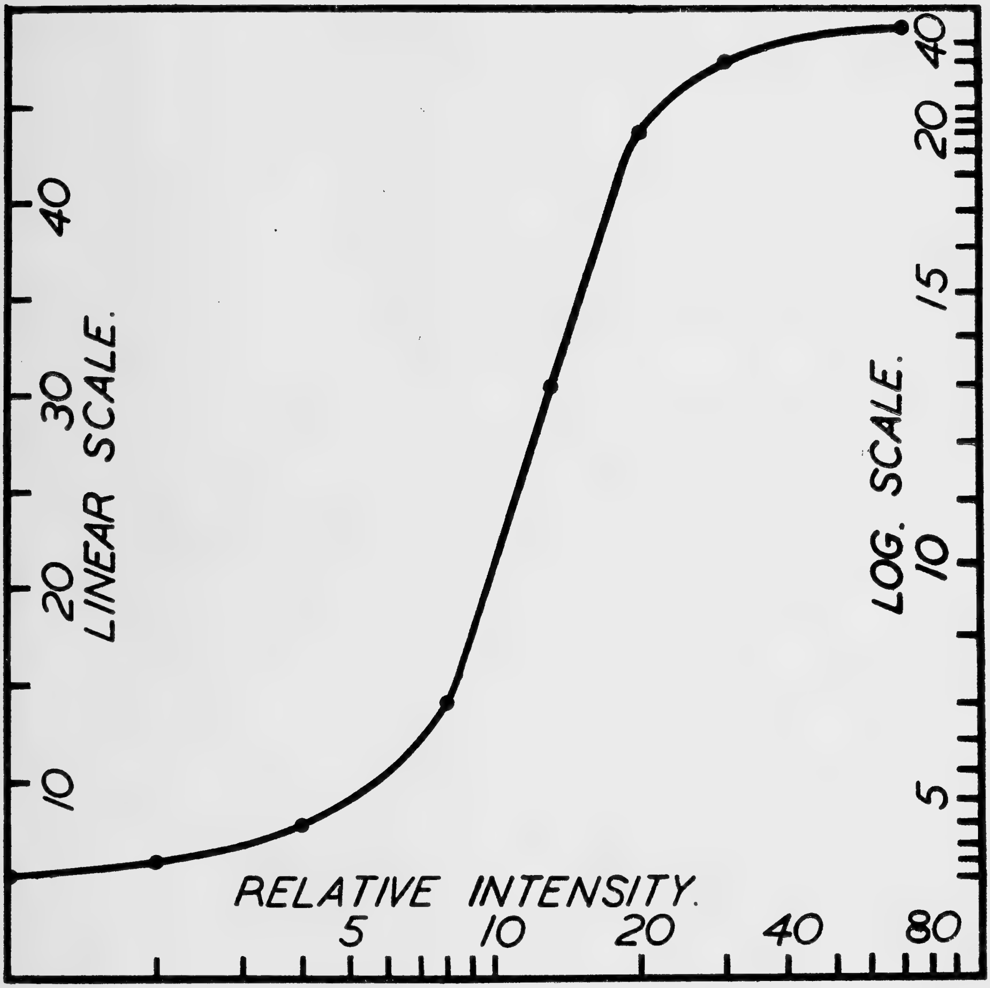

Figure 2.—Plate curve with logarithmic galvanometer scale at the right-hand ordinate.

represents a logarithmic galvanometer scale constructed to fit the plate characteristic (Sinclair, 1945). If the microphotometer be adjusted to give full scale deflection when an opaque card is placed over the plate and zero deflection at a clear section of the plate, the galvanometer spot of light reads log intensity directly on the log scale, thereby increasing the speed of determinations, eliminating one source of arithmetical error and increasing the accuracy in low density regions.

Analytical Procedure.

Sampling.

Filings that pass a 100 mesh sieve were prepared with either a " dead-smooth warding file " or with a 120 grit Alundum grinding wheel. In the latter case it is best to use a low speed wheel to avoid burning and to press the sample lightly on the wheel; separation of the filings from the wheel dust is accomplished by holding an aluminium beaker with an Alnico bar magnet inside it in the path of the dust and filings shooting off the wheel; if the beaker be upright over the top of the grinder and the sample is held so that the particles impinge on the bottom at about 45°, the filings adhere while the dust passes on; when the magnet is lifted out of the beaker the filings drop into a suitable container.

The filings are uniform enough to dispense with the sieve. To avoid weighing, filings sufficient to fill a $\frac{1}{16}$ in. hole bored to a depth of $\frac{1}{16}$ in. in a piece of brass were used as a measure; the hole holds about 15 mgm. A gain in accuracy of about 8% was obtained by working with a fixed mass of uniform filings as compared to random mass and random particle size.

Excitation

The ends of a pair of pure graphite rods are cut to the shapes illustrated in Figure 3. The cutters were made from a piece of a hacksaw blade and fixed in a brass holder bored to pass the rods; it is convenient to attach the cutters to the ends of the shaft of a small electric motor.

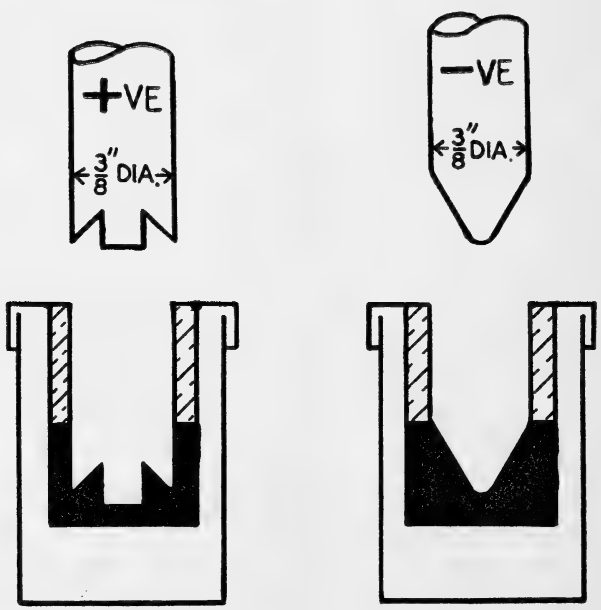

Figure 3.—Section of the electrode cutters and electrode ends.

The prepared rods are then fixed in the holders and connected in series with a reactance, a rheostat, an ammeter and a 300 volt D.C. line, the lower electrode being positive. The arc is struck by lowering the top electrode to touch the lower and then separating. The rheostat is adjusted so that the current is seven amperes when the analysis gap is initially 8 mm. All electrodes are pre-arced about 20 seconds; a concave mirror placed behind the electrodes images the arc on a screen placed beside the slit; an outline of the analysis gap is

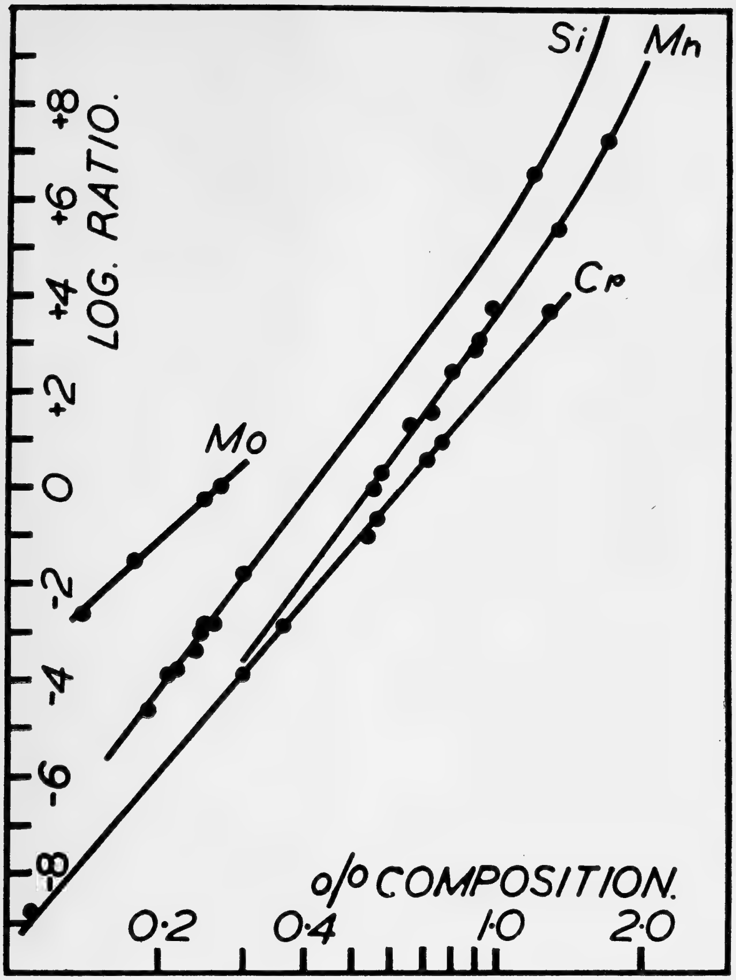

Figure 4.—Working curves for silicon, manganese, chromium and molybdenum.

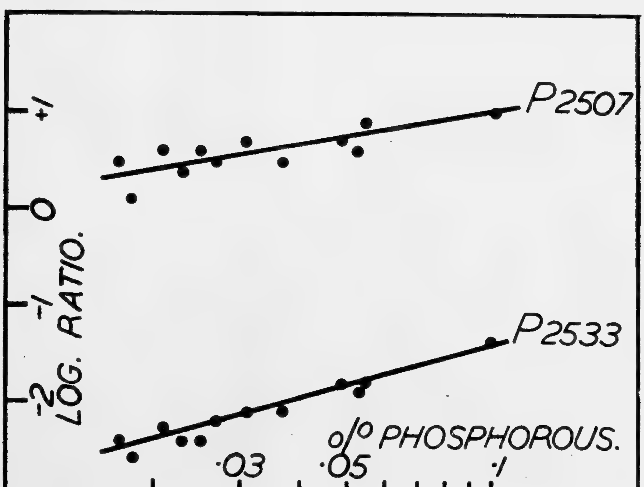

Figure 5.—Working curves for phosphorus.

marked on the screen so that the electrodes can be accurately placed in position during the pre-arcing. The prepared sample is then placed in the annulus around the centre peg of the lower electrode.

Exposure.

With the analysis gap 80 cms. from the slit the arc is allowed to run for five seconds after striking, the mirror and screen enabling the electrodes to be set the right distance apart. An exposure of one minute is then made. In this period of 65 seconds most of the sample and the centre peg are burnt away.

Analytical Curve.

The working or analytical curve exhibits the relationship between the percentage of the element and the ratio of the intensities of an element and an iron line. When plotted on log-log paper the curves are nearly straight lines over a range of concentration such that the line densities lie on the straight part of the plate curve. Different lines of the same element are employed for the different concentrations—the more intense line being employed for the lower concentrations. A stepped absorption filter may also be placed before the slit (Baker, 1934). Figures 4 and 5 illustrate the analytical curves. Table 2 gives the chemical analysis of the samples used for the preparation of these curves.

TABLE 2.

Chemical Analysis of Standard Samples.

Number.	C.	P.	Mn.	Si.	S.	Ni.	Cr.	Mo.
	%	%	%	%	%	%	%	%
1	0·64	0·053	0·91	1·92	0·032	0	0·30	0
2	·30	·037	·93	·193	·028	3·72	·78	0·25
3	·31	·027	·74	·246	·033	3·23	·72	·27
4	·62	·049	1·31	2·20	·029	0	0	0
5	·27	·018	·56	·203	·024	3·33	·67	·14
6	·43	·031	·82	·257	·022	0	1·30	0
7	·29	·025	·67	·242	·017	3·30	·73	·18
8	·17	·023	1·70	·261	·014	0	0	0
9	·27	·017	·56	·201	·013	2·66	·53	0
10	·30	·021	·73	·30	·016	3·34	·11	0

The presence or absence of chromium, molybdenum and nickel did not produce any observable differences in the line intensity ratios so that a reduction in the number of analysed standards is possible. Thus if we mix together the filings of samples number 4 and 9 in equal parts then the mixture contains 0·99% manganese and 1·20% silicon. Likewise aliquot mixtures with Armco (or Hilger HS) iron gives any desired range of concentrations. Points obtained from various aliquot mixtures of the standards amongst themselves and with pure iron conformed to the curves obtained with the standards alone at least as closely as some of the points from the standards. For the lower concentrations the aliquots appear to be somewhat better than the chemical analyses in so far as they lie more nearly on the straight line of the analytical curves. Some preliminary attempts to build up standards by adding manganese dioxide, quartz dust and chromic oxide to filings of electrolytic iron were not successful.

Some of the samples were analysed chemically again in order to check the reliability of the analyses in Table 2. The results for silicon and manganese

only, for four of the samples are listed in Table 3 and are typical. By comparing the two tables it is seen that the average difference between the original and check analyses is about 3½% and that for silicon in sample 5 almost 8%. Points from one or more elements in each of these samples were consistently well off the mean spectrographic analytical curve but when the corrections were made no point deviated by more than 5% for the metallic elements.

TABLE 3.

Chemical Analysis of Standard Samples.

Number.	Mn.	Si.
	%	%
4	1·36	2·28
5	0·58	0·218
8	1·73	0·250
9	0·56	0·208

Spectrum Lines Employed.

Manganese. The line pair Mn 2933 and Fe 2872 gave the curve labelled Mn in Figure 4. It is quite satisfactory over the concentration examined here.

Silicon. The line pair Si 2507 and Fe 2530 was employed for the construction of the curve labelled Si in Figure 4. The lines are marked on Plate VIII. Kayser's tables list a vanadium line at the same wavelength as this silicon line, but apparently no interference took place here. This line is preferred to the Si 2882 line because the latter is too intense without a filter. It was found most important to make the exposure at least 40 seconds for the high concentration silicon, presumably because of its high boiling point.

Chromium. The line pair Cr 2855 and Fe 2872 gave the curve labelled Cr in Figure 4.

Molybdenum. The line pair Mo 3170 and Fe 2872 gave a straight line connecting the four points listed for molybdenum in Table 2 only when the exposure was long enough to arc the sample to completion.

Phosphorus. In Figure 5 the top curve was obtained for the line pair P 2536 and Fe 2530 and the bottom curve for the line pair P 2553 and Fe 2530 additional samples not listed in Table 2 being used in the 0·05 to 0·1% phosphorus range. The lines are marked in Plate VIII. It is seen from the curves that the probable error of a single determination would be about 10%, an accuracy sufficient for only a few steelworks applications. It was found that the pre-arcing period must not exceed 10 seconds to attain even this accuracy, probably because the phosphorus volatilises quickly.

Carbon. Samples were arced to completion between copper electrodes, but no correlation between carbon content and intensity of either of the carbon lines 2478 and 2509 was found.

ACKNOWLEDGEMENTS.

The Automatic Large Quartz Spectrograph by Hilger employed in this investigation is the property of the Broken Hill Pty. Ltd., and was lent to this College by the management of the Newcastle works; the samples and their analyses listed in Table 2 and 20 others used for checking were supplied by

B.H.P. Some of the higher phosphorus samples (not listed) and some of the checking (Table 3) was supplied by the management of Rylands Bros.' Newcastle works.

Summary.

Adjustment of the Spectrograph. The slit is set at the optimum width by reducing its width until the central band in the diffraction image of a condensed spark between 10 s.w.g. steel electrodes covers the camera lens. It is shown that the accuracy of the determination of the line intensity ratios increases as the slit is narrowed.

Photometry. Brushing the photographic plate during development is found to give the most uniform results with dish rocking second best. The background to the spectrum of a high pressure mercury lamp is sufficiently intense to permit plate calibration by the variation of slit width method. The plate calibration curve is used to construct a logarithmic galvanometer scale for a microphotometer.

Analytical Procedure. About 20 mgm. of filings that pass a 100 mesh sieve are prepared with a file or Alundum wheel and arced to completion between specially shaped graphite rods on a 300 volt D.C. line. The probable error of a single determination of Si, Mn, Cr and Mo is 5% of the element content. Phosphorus can be estimated to within about 10%.

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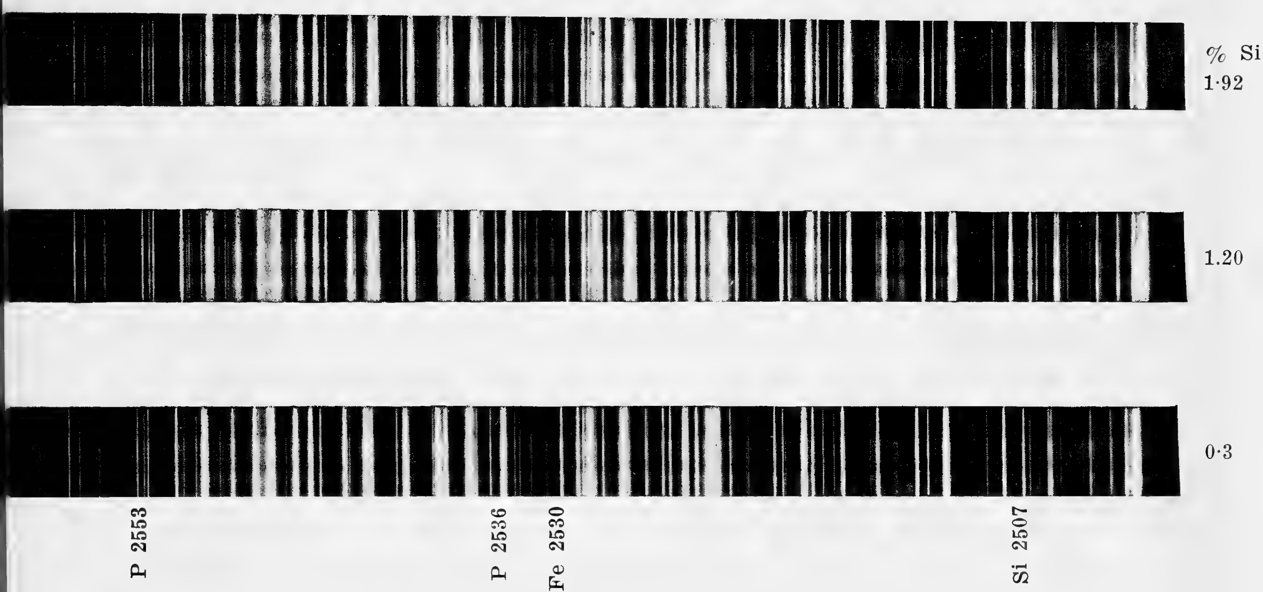
Explanation of Plate.

Both phosphorus lines and Fe 2530 are marked ; P 2536 is very close to another line but is clearly resolved on the actual spectrogram. Variation of the intensity of the silicon line 2507 with percentage of silicon is clearly visible on the spectrogram.


% Si
1·92
1.20
0·3
P 2553
P 2536
Fe 2530
Si 2507

THE URIC ACID CONTENT OF THE FEATHERS OF THE MUSCOVY DUCK (*CAIRINA MOSCHATA*).

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Recently it was found that the keratinous appendages of the integument (referred to as keratinous integument) contain large, though varying amounts of uric acid (Bolliger and Hardy, 1945; Bolliger, 1945). Most of the figures reported referred to mammals, but the uric acid contents of some isolated feathers of three birds (*Ara macac*, *Podargus strigoides* and *Gallus domesticus*) were also given. From these preliminary experiments three main questions arose:

(i) Is the uric acid content of the keratinous integument of the uricotelic birds larger and more easily detached than that of the ureotelic mammals?

(ii) Is the observed difference in the uric acid content of barbs and shafts (rhachis) and barrels (calamus) a constant feature, and is there also a difference in the uric acid content of the barrel and the shaft?

(iii) Do feathers from different locations contain different amounts of uric acid as is the case with hairs of certain mammals?

For this enquiry a readily available domestic bird, the Muscovy duck (*Cairina moschata*), was chosen.

Methods.

The following scheme of examination was adopted:

(*a*) The tip of a wing of a living duck was immersed in a comparatively large volume of water for a number of minutes and the water was subsequently examined for its uric acid content.

(*b*) Five ducks were killed by decapitation and samples of feathers from different parts of the plumage were " dry plucked " and a number of the feathers were examined under a microscope.

(*c*) Complete feathers were immersed in Folin's uric acid reagent or in a small amount of cold water for varying periods. Then the water was examined for its uric acid content.

(*d*) For series of determinations of the uric acid content of feathers and their constituents extractable by cold and hot water from different body regions, the following routine was finally followed. In a test tube complete feathers or their components, such as barbs, rhachis and calamus (usually 0·2 gm.), were left in water (usually 30 ml.) at room temperature for an hour, care being taken to wet the feathers. This was accomplished with varying success by shaking the mixture and by submerging the floating feathery particles in the water with a glass rod. Usually after a period of an hour the water was drained off and the feathers were heated in a boiling water bath for one hour with another 30 mls.

* Working under a grant from the National Health and Medical Research Council.

of fresh water. Aliquot filtered parts from the two lots of water were used for uric acid determination. In the first experiments of this series, the feathers were thoroughly defatted by boiling them with two lots of carbon tetrachloride and subsequently washing them with ether. After drying at 100° C., they were extracted several times with boiling water till no further positive tests for uric acid could be obtained. Subsequently, this defatting process was omitted and the results as listed in Table 1 refer to feathers as obtained directly from the bird.

TABLE I.

Milligrammes per Cent.

	Barbs.			Rhachis.			Calamus.			Complete Feather.		
	Cold.	Hot.	Total.	Cold.	Hot.	Total.	Cold.	Hot.	Total.	Cold.	Hot.	Total.
Feathers from												
Wing, large ..	122	17	139			34			30			
,, ,, ..	54	13	67	8	22	30	5	23	28			
,, ,, ..	90	26	116									
,, ,, ..	16	38	54									
Wing, small ..	10	41	51	6	29	35						
Upper neck ..										33	80	113
Lower neck ..	32	66	98	7	45	52*						78
Dorsum ..	12	55	67	12	35	47*						
Breast ..	36	62	98	10	44	54*						
Tail, large ..	89	45	134	9	24	33	6	12	18			
Venter " down "										32	53	85
Dorsum " pin feathers " ..										11	80	91

* In all probability the rhachis of these small feathers contains appreciable amounts of barb elements due to difficulties in dissection. The calamus is also included in these rhachides.

The results obtained by the two methods are comparable, making allowance for the drying effect of the defatting process.

Uric acid was determined by Folin's (1934) and Fearon's (1944) colorimetric methods. In addition some of the extracts were tested with the enzyme uricase as described by Blauch and Koch (1939). In two instances the chromogenic material was isolated in crystalline form and identified as uric acid.

RESULTS.

(*a*) Immersion experiments on the living animal. The distal part of the left wing of a duck which was kept as clean as possible lost 2 mg. of uric acid as indicated by the colorimetric determination of the wash water after immersion for five minutes in water at room temperature to a depth of 20 cm. After a period of one week the wing of the same animals was immersed again for five minutes to a somewhat greater depth (30 cm.) and 3 mg. of uric acid were detected in the wash water. A day after the second immersion the animal was killed. Barbs from the immersed long wing feathers contained about half as much uric acid extractable by cold water as barbs of the control wing.

(*b*) Microscopical observations. Plucked feathers from many and varied regions of the bodies of five ducks were examined under a microscope. All these feathers contained on and between the barbs and barbules both amorphous and crystalline material. The amorphous part was much greater in amount. Some

of this material was stained yellow or brown and in some instances rectangular or crystal plates showed this discoloration. When examined under polarized light a few of these crystal plates were found to be birefringent. These observations are in accordance with the assumption that these crystals are urates and that urates may also be present amongst the amorphous debris contained by the feathers.

(*c*) Extraction of uric acid at room temperature. Feathers immersed in the practically colourless uric acid test solution as described by Folin (1934) changed the colour of the solution to a blue on standing. The depth of the colour produced depends largely upon the amount of feathers immersed in a given volume of solution. Fearon's (1944) uric acid solution was found to be unsuitable for such experiments because it dyed the whole of the feather.

Water at room temperature was found to extract chromogenic material even if no attempt was made to wet the feathers. This could easily be demonstrated by adding Folin's reagent to the extracting fluid which took on a blue colour provided an adequate amount of feathers was left in the water for a sufficiently long time. For example, 3 mg. per cent. of uric acid was found to be present in the extracting water after 30 minutes of immersion of large complete feathers. After 20 hours' immersion, 15 mg. per cent. of uric acid were found to be present in the extracting water.

(*d*) Total uric acid extractable by water. The amount of urates extracted by water at room temperature from an unwetted feather is only a fraction of the total amount of uric acid present. In the example cited in the previous paragraph, another 40 mg. per cent. of uric acid were extracted with boiling water after the 20 hours extraction with cold water.

In order to obtain values for the total uric acid content of the component parts of the feather, some feathers were separated into barbs, shafts (rhachis) and barrel (calamus). The results are given in Table I. The main finding is that the shaft and the barrel contain less uric acid than the barbs. In the case of the barbs, from the long feathers of the wing and tail, more than half of the uric acid is soluble in cold water within one hour, in the majority of the cases examined. Total values found for extractable uric acid are on the average the highest of all feather components examined. In the feathers from the remainder of the body a smaller proportion of the total uric acid content is extractable by cold than by hot water.

The down gave similar results for total uric acid as the permanent small feathers, e.g., about 80 to 90 mg. per cent. The fraction extracted by cold water was also small, and ranged from 20 to 30 mg. per cent. Specially mentioned may also be the so-called pin feathers which represent the young permanent feathers still partly or completely enclosed in the sheath. They also contained about 90 mg. per cent. of total uric acid, of which less than a sixth could be extracted with cold water within one hour.

Discussion.

The aqueous extracts from the feathers of the Muscovy duck (*Cairina moschata*) contained comparatively large amounts of uric acid as indicated by the colorimetric method of Folin (1934). This has been confirmed in a number of instances with the colorimetric method of Fearon (1944), which furnished essentially the same quantitative results and which depends on a chemical principle distinct from that involved in the method of Folin. The nature of the chromogenic material has been identified as uric acid by the enzymatic method and by actual isolation of the acid.

The possibility, however, must be kept in mind that the plumage of our bird may become contaminated from the excreta, which are rich in urates.

But with the exception of the large wing and tail feathers the plumage from any part of the body including the perfectly white and well protected down and pin feathers was found to contain approximately the same amount of uric acid, e.g., 50 to 90 mg. per cent. So far no markedly higher figures were obtained from the plumage of other birds examined, and it is noteworthy that apparently the keratinous integument of the uricotelic birds does not reach the high values met with in certain ureotelic mammals, for example, the rabbit, whose hairs may contain as much as 500 mg. of uric acid (Bolliger and Hardy). Barbs from the large wing and tail feathers of the Muscovy duck frequently showed higher uric acid values (100 to 140 mg. per cent.) than those from the smaller sized constituents of the plumage.

The immersion experiments on plucked intact feathers as well as on the plumage of the living duck indicate that cold water readily extracts even without markedly wetting uric acid from the plumage of the Muscovy duck. This is particularly marked in the large wing and tail feathers, which are frequently characterized by a high total uric acid content. Since the Muscovy duck usually lives on and in the water, these findings indicate that uric acid is bound to be dissolved out from the plumage in considerable amounts and it can readily be envisaged that something of the order of 100 mg. of urates could be removed in 24 hours provided this amount was available over such a period.

In addition, the loss of urates by the process of shedding feathers, particularly in the moulting season, would also have to be assessed in order to get a full picture of uric acid loss through the integument.

It is generally accepted that barbs and rhachis are of different origin (Lillie, 1942), and this also finds its expression in the lower uric acid content of the rhachis as compared with the barbs, a fact previously pointed out (Bolliger, 1945). Anatomically complete dissection of the barbs from the shaft is difficult and has not been attempted in the small feathers, and consequently some of our present figures may be somewhat too high, since they still may contain barb elements.

The uric acid content of the calamus sometimes appears to be still lower than that of the rhachis, and this may be probably due to the fact that the calamus is entirely free of barb elements.

The values for a given type of feather may fluctuate considerably in different animals and sometimes even in the same bird. This may be explained by the ease with which uric acid is removed from the plumage and may depend on the environment and habits of the duck as well as its diet and age.

In the uricotelic birds the presence of large amounts of uric acid in the keratinous integument may be expected, and this has been proven in the present communication for a typical representative. Compared with mammals, however, there is a difference, inasmuch as the uric acid in a bird may be more easily removed by cold water than that present in the hairs of mammals. Our test animal is a water bird which, however, is also capable of existing even if no facilities for bathing are available. In these instances where no water is available, it may be surmised that the removal of the solid and finely divided urates takes place with the emanation of dust from the feathers. This undoubtedly is aided by the flapping of wings, baths in the soil and preening. In a similar manner uric acid may be constantly removed from the plumage of non-water birds and the urate—containing dust is sometimes readily visible, as for example, in the cockatoo and other parrots.

Summary.

The barbs of the feathers of *Cairina moschata*, the Muscovy duck, were found to contain from 51 to 139 mgm. per cent. of uric acid, of which a widely varying

amount, averaging from 12 to 122 mgm. per cent., is removed within an hour by cold water.

The high values of total as well as cold water-extractable uric acid occurred in the large wing and tail feathers.

The rhachis and calamus contained less uric acid than the barbs, the total amount of extractable uric acid ranging from 30 to 54 mgm. per cent. and the cold water-extractable uric acid ranging from 6 to 12 mgm. per cent.

Evidence has been presented indicating that this bird may lose considerable amount of uric acid when in the water.

The uric acid content of the plumage of this bird and others tested is not as high as that found in a number of mammals. Sometimes, however, it seems to be more easily detachable than from the hairs of mammals. This applies particularly to the large wing and tail feathers.

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THE CHEMISTRY OF OSMIUM.

PART II. THE REDOX POTENTIAL OF A TRIVALENT-QUADRIVALENT OSMIUM COUPLE IN HYDROCHLORIC ACID SOLUTION.

By F. P. DWYER, D.Sc.,
J. E. HUMPOLETZ
and R. S. NYHOLM, M.Sc.

Manuscript received November 4, 1946. Read December 4, 1946.

In a previous paper (Dwyer, McKenzie and Nyholm, 1946), the potential of the trivalent-quadrivalent osmium couple in hydrobromic acid solution was determined as $+0 \cdot 452$ volt at zero acid concentration. This information suggested that the reduction of potassium hexachlorosmate (K_2OsCl_6) could also be effected using silver wool, provided that the concentration of hydrochloric acid was kept low enough. The reaction involved would be:

$$OsCl_6^{=} + Ag + Cl^{-} \rightleftarrows OsCl_6^{\equiv} + AgCl \downarrow$$

The effect of hydrochloric acid is obvious from Table I; this shows that as the molar concentration of hydrochloric acid increased, the difference between the potentials of the $OsCl_6^{\equiv}/OsCl_6^{=}$ and the Ag/AgCl systems rapidly diminishes. The redox potentials differ by $0 \cdot 2$ volt in 1 N HCl and only by $0 \cdot 14$ volt in 5 N HCl. Since it is generally agreed that a difference of at least $0 \cdot 2$ volt between two systems is necessary to effect an analytically complete reaction, the concentration of acid used during reduction must be kept fairly low.

TABLE I.

E_0 Value in	System.	
	Ag/AgCl.	$OsCl_6^{\equiv}/OsCl_6^{=}$.
1 M HCl	$+0 \cdot 2222$ volt	$+0 \cdot 416$ volt
5 M HCl	$+0 \cdot 164$,,	$+0 \cdot 307$,,

Estimated taking $f_{\pm}$ for 5 M HCl$=2 \cdot 0$.
Latimer (1938).

Reduction of the quadrivalent osmium complex using silver wool was found to be satisfactory and the potential of the $OsCl_6^{\equiv}/OsCl_6^{=}$ system in various concentrations of hydrochloric acid was then determined by the method of mixing.

Although some doubt exists as to the correct formulation of the Os (III) and Os (IV) ions in solution, the expressions $OsCl_6^{\equiv}$ and $OsCl_6^{=}$ will be used in this paper to indicate the ion derived from these complex ions whether it be the true hexachloro ion or one of its hydrolysis products, such as OsO^{+} and OsO^{++}. (See below.)

The results obtained are shown in Table II and Fig. 1.

In Fig. 1 the graph of the system $OsBr_6^{\equiv}/OsBr_6^{=}$ is added for comparison. Within the limits of experimental accuracy, the same extrapolated value for

TABLE II.

Effect of Hydrochloric Acid on the System $OsCl_6^{=}/OsCl_6^{\equiv}$.

HCl Concentration.	E_0.	HCl Concentration.	E_0.
0·1 Molar	$+0{\cdot}446_4$ volt	2·0 Molar	$+0{\cdot}387_0$ volt
0·2 ,,	$+0{\cdot}442_1$,,	3·5 ,,	$+0{\cdot}337_1$,,
0·5 ,,	$+0{\cdot}429_6$,,	5·0 ,,	$+0{\cdot}306_9$,,
1·0 ,,	$+0{\cdot}416_1$,,		

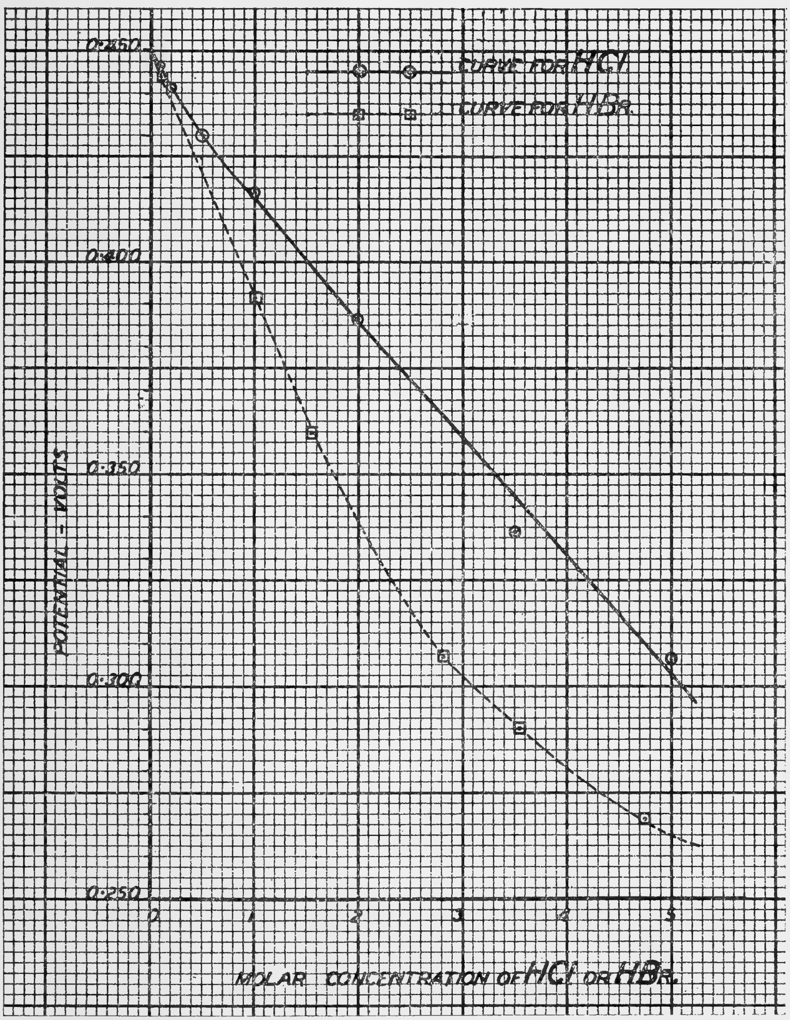

Figure 1.

E_0 at zero acid concentration is found for both chloride and bromide systems. The shape of the curves indicates that the systems are essentially cationic. The E_0 values for cationic systems such as Fe^{++}/Fe^{+++} and Cr^{++}/Cr^{+++} increase with decreasing ionic strength, whilst E_0 values for anionic systems such as $Fe(CN)_6^{\equiv}/Fe(CN)_6^{\equiv}$ decrease as the ionic strength falls. This negative value for dE_0/dI suggests that the osmium ionic species are primarily cations rather than anions in spite of the fact that the solutions were made up from the substance K_2OsCl_6. A possible explanation of this phenomenon is that as the acid concentration falls, ions of the type OsO^+ and OsO^{++} are formed.

Thus, $OsCl_6^{-} + H_2O \rightleftarrows OsO^+ + 2H^+ + 6Cl^-$

and $OsCl_6^{=} + H_2O \rightleftarrows OsO^{++} + 2H^+ + 6Cl^-$.

These equilibria would be displaced to the left with increasing acid concentration. The formation of these ions at low acid concentrations would explain why the same E_0 value is obtained at zero acid concentration for both bromosmate and chlorosmate systems since the same cations would be formed in each case.

The effect of chloride ions on the potential lends support to the above hypothesis. Addition of sufficient potassium chloride to the $OsCl_6^{=}/OsCl_6^{\equiv}$ system in 2 N hydrochloric acid to give a chloride concentration of 3 N results in a potential of $0 \cdot 380_6$ volt. The potential for 3 N hydrochloric acid is 0·356 volt. This indicates that a raising of the potential is more readily effected by chloride ions than by hydrogen ions, that is, the system is rendered less cationic by adding chloride ions. This would be expected from applying the law of mass action to the above equilibria.

It may be observed that the E_0 value of the bromosmate system falls much more rapidly than the chlorosmate with increasing acid concentration. This might be explained by assuming a greater stability of the $OsBr_6^{=}$ ion over the corresponding $OsCl_6^{=}$ ion, which would affect the active ratio of oxidant to reductant differently in each case.

From the graph the value +0·452 volt has been obtained as the extrapolated standard oxidation reduction potential for the $OsCl_6^{\equiv}/OsCl_6^{=}$ system in hydrochloric acid solution.

Experimental.

Preparation of Solutions.

Potassium Hexachlorosmate (K_2OsCl_6).

Osmium tetroxide was converted into potassium osmyl oxynitrite (Dwyer, McKenzie and Nyholm, *ibid.*) and the latter boiled with concentrated hydrochloric acid ; orange red cubes and octahedra of the required compound were precipitated on cooling. The stock solution of M/100 K_2OsCl_6 was made up by dissolving the required weight of K_2OsCl_6 in N/10 hydrochloric acid.

Potassium Hexachlorosmite (K_3OsCl_6).

To half of the solution prepared above was added sufficient solid potassium chloride to give the amount of potassium required for the K_3OsCl_6 salt. The solution was freed from air by passing a stream of air-free carbon dioxide and was then placed at room temperatures in the apparatus containing silver wool as previously described by Dwyer, McKenzie and Nyholm (*ibid.*). The mixture was stirred occasionally with air-free carbon dioxide and allowed to stand for four days, when all the silver chloride had precipitated out, the solution having changed colour from yellow to brownish yellow.

Completeness of reduction was tested for by potentiometrically titrating the K_3OsCl_6 into approximately N/100 ferric sulphate in sulphuric acid. 4·0 ml. of 0·00983 N ferric sulphate in N/2 sulphuric acid containing 10 ml. 2·12 N hydrochloric acid required 3·95 ml. M/100 K_3OsCl_6. The latter figure was the mean of three titrations. All titrations were carried out in an atmosphere of air-free carbon dioxide. Since the theoretical figure for the above titration is 3·93 ml., completeness of reduction is indicated. These results have been plotted in Fig. 2 ; from this graph a

value of E_0 at the ionic strength used equal to $+0 \cdot 449$ volt is obtained. As the figure obtained by the method of mixing at the same chloride ion concentration is $+0 \cdot 418$ volt, the unreliability of the potentiometric titration method for determining E_0 values is emphasised.

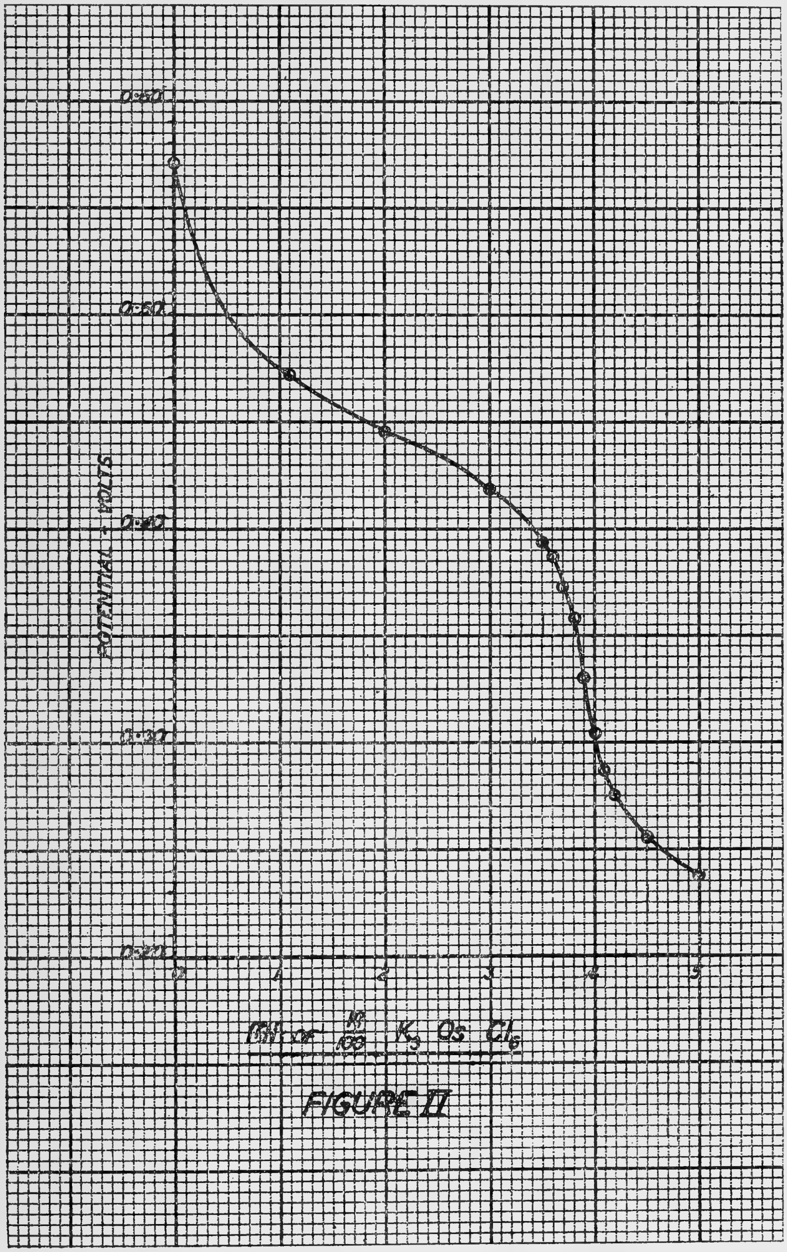

FIGURE II

Experimental Procedure.

5 ml. $OsCl_6^{=}$ solution together with the correct amount of hydrochloric acid and a little distilled water were heated to boiling point to remove air and the solution cooled to 0° C. with carbon dioxide passing. This process was repeated,

the solution diluted to 25 ml. with air-free water, and then 5 ml. $OsCl_6^{\equiv}$ solution from an air-free burette added, the whole solution being placed in the four-neck flask already described (Dwyer, McKenzie and Nyholm, *ibid.*). The mixture was allowed to stand in contact with a rhodium electrode for 48 hours in an atmosphere of carbon dioxide. The carbon dioxide was freed from oxygen by two traps containing acid-titanous chloride ; chromous chloride could not be used as it evolved hydrogen which gradually reduced the $OsCl_6^{=}$ at the rhodium surface.

Potentials of systems at low acid concentrations were found to rise to equilibrium whilst those containing high concentrations of acid fell to equilibrium. These facts were observed with the bromosmate system also.

All measurements were carried out at 20° C. using a Leeds and Northrup Type K potentiometer. The thermostat was controlled to $\pm 0 \cdot 1°$ C. A saturated calomel half cell was used as reference electrode, contact with the redox cell being made through a saturated potassium chloride agar-agar bridge. The potential of the calomel half cell was taken as $+0 \cdot 2476$ volt at the temperature of the experiment, 20° C.

Equilibrium was reached as a rule after 48 hours, the potential then remaining constant for several days.

It was found that care was essential in handling solutions of K_3OsCl_6 in dilute acids because absorption of oxygen occurred readily forming a dark brown solution containing what was probably the oxycomplex of formula $K_2(OsO_2Cl_4)$. In the presence of high concentrations of acid oxidation to K_2OsCl_6 takes place.

Summary.

The oxidation reduction potential of the trivalent-quadrivalent couple in hydrochloric acid increases with decreasing acid concentration, giving an extrapolated value for the standard oxidation reduction potential at zero acid concentration of $+0 \cdot 452$ volt. The system is compared with the same couple in hydrobromic acid solution.

References.

Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., 1946. This Journal, **79**, 183.

Latimer, W., 1938. Oxidation Potentials, p. 177. (Prentice Hall.)

Department of Chemistry,
University of Sydney,
and
Department of Chemistry,
Sydney Technical College.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 3, 1946.

The Annual Meeting, being the six hundred and thirtieth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Dr. A. Bolliger, was in the chair. Forty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

F. LIONS, B.Sc., Ph.D., A.R.I.C.

Vice-Presidents :

A. BOLLIGER, Ph.D., A.A.C.I.
J. A. DULHUNTY, D.Sc.
H. H. THORNE, M.A., B.Sc., F.R.A.S.
A. B. WALKOM, D.Sc.

Hon. Secretaries :

D. P. MELLOR, D.Sc., F.A.C.I.
F. R. MORRISON, A.A.C.I., F.C.S.

Hon. Treasurer :

G. D. OSBORNE, D.Sc., Ph.D.

Members of Council :

R. L. ASTON, B.Sc., B.E., M.Sc., Ph.D., A.M.I.E. (*Aust.*).
R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*), Ph.D. (*Camb.*), F.A.C.I., F.Inst.P.
R. O. CHALMERS, A.S.T.C.
H. O. FLETCHER.
F. N. HANLON, B.Sc.
P. HINDMARSH, M.A., B.Sc.Agr.
R. S. NYHOLM, M.Sc.
D. J. K. O'CONNELL, S.J., M.Sc., F.R.A.S.
J. L. STILL, B.Sc., Ph.D.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and, on the recommendation of Dr. G. D. Osborne, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1946.

LIABILITIES.

1945. £		1946. £	s.	d.	£	s.	d.
126	Accrued Expenses				245	17	6
15	Subscriptions Paid in Advance				13	2	6
81	Life Members' Subscriptions—Amount carried forward				68	0	0
	Trust and Research Funds (detailed below)—						
1,855	Clarke Memorial	1,875	2	5			
1,051	Walter Burfitt Prize	1,030	12	10			
700	Liversidge Bequest	725	15	0			
3,149	Research	3,247	15	0			
					6,879	5	3
25,708	ACCUMULATED FUNDS				25,774	18	6
	Contingent Liability—in connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—						
(902)	Maximum Liability £901 16s. 8d.						
£32,685					£32,981	3	9

ASSETS.

1945. £		1946. £	s.	d.	£	s.	d.
926	Cash at Bank and in Hand				343	15	9
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—						
	Held for—						
	Clarke Memorial Fund	1,800	0	0			
	Walter Burfitt Prize Fund	1,000	0	0			
	Liversidge Bequest	700	0	0			
	Research Fund	3,000	0	0			
	General Purposes	4,160	0	0			
9,760					10,660	0	0
—	Prepayment				26	15	0
	Debtors for Subscriptions	50	8	0			
	Deduct Reserve for Bad Debts	50	8	0			
					—		
14,756	Science House—One-third Capital Cost				14,715	0	0
6,800	Library—At Valuation				6,800	0	0
397	Furniture—At Cost—*less* Depreciation				392	16	6
34	Pictures—At Cost—*less* Depreciation				31	16	6
12	Lantern—At Cost—*less* Depreciation				11	0	0
£32,685					£32,981	3	9

TRUST AND RESEARCH FUNDS.

	Clarke Memorial.			Walter Burfitt Prize.			Liversidge Bequest.			Research.		
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
Capital at 28th February, 1945 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 28th February, 1945	54	16	5	51	10	0	—			148	10	0
Interest for twelve months ..	64	13	9	29	2	10	25	15	0	99	5	0
	119	10	2	80	12	10	25	15	0	247	15	0
Deduct Expenditure ..	44	7	9	50	0	0	—			—		
Balance at 28th February, 1946 ..	£75	2	5	£30	12	10	£25	15	0	£247	15	0

ACCUMULATED FUNDS.

	£	s.	d.
Balance at 28th February, 1945	25,707	11	11
Add Surplus for twelve months (as shown by Income and Expenditure Account) ..	72	11	7
	25,780	3	6
Less Increase in Reserve for Bad Debts ..	5	5	0
	£25,774	18	6

G. D. OSBORNE,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1946, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 20th March, 1946.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1945, to 28th February, 1946.

1944-5. £		1945-6. £ s. d.	£ s. d.
308	To Printing and Binding Journal—Vol. 78	492 5 0	
310	,, Salaries	309 10 0	
30	,, Library—Purchases and Binding	145 5 9	
113	,, Printing—General	49 7 5	
63	,, Miscellaneous	171 2 8	
66	,, Postage and Telegrams	63 4 5	
47	,, Rent—Science House Management Committee	42 8 8	
34	,, Cleaning	37 0 0	
24	,, Depreciation	23 7 0	
19	,, Telephone	18 8 1	
15	,, Insurance	14 17 10	
13	,, Audit	12 12 0	
9	,, Electricity	8 9 5	
1	,, Repairs	0 5 0	
1,052			1,388 3 3
305	,, Surplus for Twelve Months		72 11 7
£1,357			£1,460 14 10

1944-5. £		1945-6. £ s. d.	£ s. d.
459	By Membership Subscriptions		477 15 0
400	,, Government Subsidy		400 0 0
360	,, Science House—Share of Surplus		425 0 0
120	,, Interest on General Investments		130 19 0
	,, Receipts from Reprints	36 14 1	
15	*Less* Expenditure	23 11 6	
			13 2 7
3	,, Other Receipts		0 18 3
—	,, Proportion of Life Members' Subscriptions		13 0 0
£1,357			£1,460 14 10

The Annual Report of the Council (1945–46) was read, and on the recommendation of Professor Elkin, adopted.

Report of the Council, 1945–1946 (Rule XXVI).

We regret to report the loss by death of seven members since April 1st, 1945: Thomas Hodge-Smith (1922), Richard Old (1903), Edward Sutherland Stokes (1909), Frederick Stapleton Mance (1924), Leslie Vickery Waterhouse (1924), John Powell (1918), Allan Clunies Ross (1928), and also of an honorary member, James T. Wilson (1922).

By resignation the Society has lost six members: Mrs. A. V. M. Thomas, J. S. Burkitt, H. Finnemore, Sir Ernest T. Fisk, Professor V. M. Trikojus and Professor J. C. Earl.

The membership now stands at 300, 23 new members having been elected during the year, namely, Frederick William Ayscough, Norma Dorothy Laing, Barbara Wright, Harold Burnell Carter, Leonard Luber, Lyndon Charles Noakes, Jack Lehane Willis, Ronald Arthur Eade, John Seymour Proud, Laurence Gordon Walters, Evelyn May Webster, Arthur Roylance Coombes, Samuel Morris, Alwyn Walker Prescott, Alan Charles Higgs, Jean Armytage, Phyllis Margaret Rountree, Hellmut Friedrich Furst, Pauline Mary Sambell, Aileen Sampson, Albert Shulman, Leslie Lionel Hall and Lewis Michael Simmons.

Eleven ordinary meetings of the Council and one special meeting were held during the year beginning April 1st, 1945, at which the average attendance was 17. During the same period nine general monthly meetings were held, with an average attendance of 51 members.

Twenty-two papers were accepted for reading and publication during the year, and the following short talks were given :

" Organisation of Science in the United States and its Relationship to Australian Science through a Scientific Liaison Officer ", by Mr. N. A. Whiffen, A.A.C.I.
" Aerial Infection ", by Miss P. M. Rountree, M.Sc., Dip.Bac.
" Indonesia ", by Mr. J. B. D. Pennink, Consul-General for the Netherlands.
" Great Telescopes ", by H. W. Wood, M.Sc.

Exhibits.—" Transmuted Wood ", by Dr. D. P. Mellor ; " X-Ray Tubes ", by Mr. B. W. Scott ; and " Light Figures used in the Orientation of Quartz Sections ", by Miss F. M. Quodling.

Films.—Two films were shown by courtesy of the Netherlands-Indies Government Information Service, namely " Indonesian Harmony " and " Deliveration of the Indies ".

Symposia.—At the monthly meeting held in August, a symposium on " Fluorine " was held, the following being the speakers and subjects :

" Inorganic Compounds of Fluorine ", by Dr. D. P. Mellor.
" Fluorine in Organic Chemistry ", by Dr. F. Lions.
" Fluorine in Dental Health ", by Dr. N. E. Goldsworthy.

Much interest was taken in this subject, 70 members and visitors being present.

In the following month the general meeting was again devoted to a symposium, this time the subject being " Visual Education ". Squadron-Leader N. Rosenthal opened the discussion, illustrating his talk with the following films :

" Principles of Radar."
" The Heart and Circulation of the Blood."
" The Electron."
" The Symphony Orchestra."
" Diary of a Sergeant (Medical Rehabilitation)."

This was followed by a short address by Mr. J. C. Storey. This meeting was attended by 104 members and visitors.

Commemoration of Great Scientists.—The December general monthly meeting was devoted to the commemoration of great scientists, and the following addresses were given :

" Alessandro Volta ", by Dr. David Myers.
" Wilhelm Roentgen ", by Professor O. U. Vonwiller.
" Institution of the Alfred Nobel Prize ", by Dr. D. P. Mellor.

Popular Science Lectures.—This year only four of the five Popular Science Lectures arranged were delivered, these taking place in the months of June, July, September and November. The lecture for August was indefinitely postponed because of the cessation of hostilities and the consequent public holidays, and the last lecture of the series was given in November instead of October because of the lack of lighting facilities caused by strikes. The lectures were well attended by both members of the Society and the general public.

June 21st.—" The Chemistry of Water and Washing ", by R. S. Nyholm, M.Sc.
July 19th.—" Penicillin and its Medical Uses ", by Jean Armytage, M.B., B.Sc., M.R.A.C.P.
September 20th.—" The Mediterranean—Past and Future ", by Professor A. H. McDonald, M.Sc., Ph.D.
November 15th.—" Liquid Life ", by Professor G. G. McDonald, B.Sc., Ph.D.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1945 was delivered by Professor E. S. Hills, D.Sc., Ph.D., on June 13th, the title being " Some Aspects of the Tectonics of Australia ".

Clarke Memorial Medal.—The Clarke Memorial Medal for 1945 was awarded to Professor W. N. Benson, of the University of Otago, Dunedin, New Zealand, for his contribution to geology.

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Society greatly appreciates the Government's continued interest in its activities.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition. During 1945, £900 was invested in war loans.

Election of Councillor.—At the Council meeting held in October, Dr. R. C. L. Bosworth was elected to Council in place of Mr. A. Maccoll, who had left for England in pursuance of his research work, having been awarded an Imperial Chemical Industries Fellowship.

Royal Society, London.—A letter was received from the Royal Society, London, stating that now the war was over, the commemorative celebrations in honour of Sir Isaac Newton would be held in July, 1946. It was decided to ask Dr. Edgar Booth and Mr. A. Maccoll to represent the Society at the Conference.

Annual Dinner.—With the end of the war it was resolved to hold an Annual Dinner on March 28th, 1946, at the Union Refectory, University of Sydney. There were 117 present ; Professor Eric Ashby was guest of honour, and the Minister for Education, the Honourable R. J. Heffron, represented the Premier and Parliament.

Section of Industry.—It was decided to revive the Section of Industry now that hostilities have ceased.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1945, to February 28th, 1946, has been £410.

Science House Management Committee.—The Royal Society has had as its representatives at the meeting of the Management Committee of Science House, Dr. G. D. Osborne and Mr. F. R. Morrison, with Mr. Allan Clunies Ross and Mr. H. H. Thorne as substitute representatives.

Science House Extension Committee.—It was decided to appoint Dr. G. D. Osborne and Mr. E. J. Kenny the two representatives for the Royal Society with power to enter into preliminary discussion with the other owner-bodies. Mr. Kenny's place was later taken by Dr. A. Bolliger. A special sub-committee was formed to make suggestions to the two representatives: these suggestions included one central library and reading room for Science House, a large lecture hall and a greater number of offices in the enlarged building.

The Library.—The amount of £28 10s. 3d. has been expended on the purchase of periodicals, and the amount of £82 is being spent on binding; the amount being spent on the library is therefore £110 10s. 3d.

Exchanges.—The number of volumes now being sent to other societies is 239.

Borrowers and Readers.—Members and visitors reading in the library numbered 21.

The number of books and periodicals borrowed by members, institutions and accredited readers was 241.

Among the institutions which made use of the arrangements for inter-library borrowing were: Fisher Library, National Standards-Radiophysics Library, Standards Association of Australia, Metropolitan Water, Sewerage and Drainage Board, C.S. and I.R. Food Preservation Laboratory, Homebush, Irrigation Commission, Canberra National Library, McMaster Animal Health Laboratory, C.S. and I.R. Fisheries, Cronulla, Department of Public Works, Geology Department of the University of Sydney, Elliotts and Australian Drug Company, Australian Chemical Institute, Colonial Sugar Refining Company Ltd., Department of Labour and National Service, and the Australian Glass Manufacturers.

Increased Circulation of the "Journal and Proceedings".—With a view to increasing the circulation of the Society's "Journal and Proceedings", and in accordance with a scheme proposed by the Honorary Editorial Secretary, specimen copies have been sent to 26 institutions and societies in Canada and the United States of America.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1946 to Mr. J. M. Black.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1946 would be delivered by Professor L. A. Cotton, the title of the lecture being "The Pulse of the Pacific".

Liversidge Lecture.—It was announced that the Liversidge Lecture for 1946 would be given by Dr. L. H. Briggs of Auckland University College, some time in August.

Election of Auditors.—On the motion of Mr. R. W. Challinor, seconded by Mr. R. S. Nyholm, Messrs. Horley & Horley were re-elected as Auditors to the Society.

Library.—The following donations were received: 318 parts of periodicals, 11 whole volumes and 426 back numbers.

The following paper was read by title only: "Deep Focus Earthquakes", by D. J. K. O'Connell, S.J., M.Sc., F.R.A.S.

The President, Dr. A. Bolliger, delivered his Presidential Address, the second part of which was entitled "Some Aspects of Marsupial Reproduction".

Dr. Bolliger then installed Dr. F. Lions as President of the Society for the year 1946–1947. Dr. Lions expressed his appreciation of the honour conferred on him, and then asked Professor H. Priestley to move a vote of thanks to the retiring President. Dr. Lions also referred to the services of Professor A. P. Elkin, who was retiring from the position of Honorary Secretary after nearly eight years' service, and asked Professor Priestley to include Professor Elkin in the vote of thanks. Professor Priestley said that the subject of the Presidential Address was a very important one, especially to Australia. The vote of thanks to Dr. Bolliger and to Professor Elkin was carried.

A. BOLLIGER, President.

May 1st, 1946.

The six hundred and thirty-first General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Forty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Ernst Herbert Blaschke and Norma Winifred Donohoo.

Popular Science Lecture.—It was announced that the first Popular Science Lecture for 1946 would be given by H. O. Fletcher on Thursday, May 16th, at 8 p.m., and would be entitled "Extinct Monsters".

Library.—The following donations were received: 117 parts of periodicals, two whole volumes and 77 back numbers.

The following papers were read:

"Deep Focus Earthquakes", by D. J. K. O'Connell, S.J., M.Sc., F.R.A.S.

"A Simple Demonstration of the Difference between Film and Nuclear Boiling", by R. C. L. Bosworth, Ph.D., F.A.C.I.

Lecturettes.—The following lecturettes were given:

"Australian Gem Stones", by R. O. Chalmers, A.S.T.C.

"Synthetic Diamond", by D. P. Mellor, D.Sc., F.A.C.I.

June 5th, 1946.

The six hundred and thirty-second General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Nineteen members were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Henry Gordon Farnsworth, a member since 1921.

The certificates of eight candidates for admission as ordinary members of the Society were read for the first time.

In the absence of a quorum, the election of members, whose certificates were to be read for the second time, was postponed until a future meeting.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1946 would be given by Professor L. A. Cotton, M.A., D.Sc., on Thursday, June 20th, 1946, at 8 p.m., and would be entitled "The Pulse of the Pacific".

Library.—The following donations were received: 146 parts of periodicals, three whole volumes and 173 back numbers.

Correspondence.—Circular from the Australian Chemical Institute *re* conjoint meeting of Sydney Chemical Societies was read. Also an invitation from the Australian Association of Scientific Workers to a meeting to be held on Wednesday, June 12th.

The following papers were read:

"Physical Changes Accompanying the Drying of Australian Lignites", by J. A. Dulhunty, D.Sc.

"The Instability Constant of the Tris-Orthophenanthroline Ferrous Ion", by F. P. Dwyer, D.Sc., and R. S. Nyholm, M.Sc.

"Derivatives of 2 : 3-Diphenyl Indole", by E. Ritchie, M.Sc.

Lecturette.—Owing to the limited time available, Dr. Bosworth had kindly consented to postpone his lecturette until a future meeting.

July 3, 1946.

The six hundred and thirty-third General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Twenty-five members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as ordinary member of the Society was read for the first time.

Election of Members.—In view of the fact that less than 20 members were present, the President invoked the wartime rule that the votes of at least 12 members were sufficient for the election of new members.

The following members, whose certificates had been read for the second time, were duly elected to membership: Gordon Alfred Barclay, Keith Edward Bullen, Rodney Thomas Cook, Ernest John Jasper Harrison, Nora Hinder, Guy Frederick Johnson, Charles St. John Mulholland, Helen May McRoberts, Norman Pinwill, Bryce Harrison Potter, Beryl Scott and Ifor Morris Thomas.

Popular Science Lecture.—It was announced that the Popular Science Lecture for July would be delivered by Professor W. M. O'Neil, M.A., on Thursday, July 18th, at 8 p.m., and would be entitled "A New Road for the Disabled Soldier".

Library.—The following donations were received: 150 parts of periodicals, one book and 92 back numbers.

Correspondence.—Circular from Sydney University Extension Board *re* course of lectures on Statistics by Miss Helen Newton Turner was read.

Paper.—In the absence of the authors, the President gave a short summary of the following paper:

"Some Disubstituted Diphenyl Derivatives", by W. J. Dunstan, B.Sc., and G. K. Hughes, B.Sc.

Lecturettes.—The following lecturettes were given:

"Some Recent Advances in Cellular Metabolism", by J. L. Still, B.Sc., Ph.D.
"New Instruments of Scientific Interest", by D. P. Mellor, D.Sc., F.A.C.I.

August 7th, 1946.

The six hundred and thirty-fourth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Fifty-three members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Norman Richard Wyndham.

Liversidge Research Lectures.—It was announced that the Liversidge Research Lectures for 1946 would be delivered by L. H. Briggs, D.Phil. (Oxon.), D.Sc. (N.Z.), F.N.Z.I.C., F.R.S.N.Z., on Monday and Tuesday, August 12th and 13th, at 8 p.m., and would be entitled "Plant Products of New Zealand, Parts I and II".

Popular Science Lecture.—It was announced that the next Popular Science Lecture would be given by A. R. Penfold, F.A.C.I., F.C.S., on Thursday, August 15th, 1946, at 8 p.m., and would be entitled "Recent Developments in Plastics".

Library.—The following donations were received: 125 parts of periodicals and 72 back numbers.

Correspondence.—Letter from Dr. E. H. Booth, advising that Mr. A. Maccoll and the writer had represented the President of the Royal Society of New South Wales at the Newton Tercentenary Celebrations in London on July 15th. The celebrations had proved very successful.

The following papers were read by title only:

"Stratigraphy of Western Australia", by C. Teichert, D.Sc. (Communicated by Dr. W. R. Browne.)
"An Occurrence of Synthetic Nepheline", by A. J. Lambeth, B.Sc.
"Major Shallow Earthquakes, 1909–1911", by D. J. K. O'Connell, S.J., M.Sc., F.R.A.S.

Symposium.—A symposium, arranged by Dr. D. P. Mellor, was held on "Power Resources of the Commonwealth". The following short addresses were given:

"Fuel Energy", by J. A. Dulhunty, D.Sc.
"Solar Energy", by T. Iredale, D.Sc., F.R.I.C.
"Atomic Energy", by R. B. Makinson, B.Sc., Ph.D.

September 4th, 1946.

The six hundred and thirty-fifth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Thirty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Bruno Breyer and Felix Gutmann.

Patron of Society.—It was announced that His Excellency the Governor of New South Wales, Lieutenant-General John Northcott, C.B., M.V.O., had granted his patronage to the Society.

Popular Science Lecture.—It was announced that the next Popular Science Lecture would be given by Miss P. M. Rountree, M.Sc., Dip.Bact., on Thursday, September 19th, 1946, at 8 p.m., and would be entitled "The Smallest of Life-Virus".

Library.—The following donations were received: 135 parts of periodicals, 11 books and 101 back numbers.

Correspondence.—Letter from Mr. A. Maccoll furnishing some details of the Newton Tercentenary Celebrations, at which he and Dr. E. Booth represented the Royal Society of New South Wales.

The following papers were read :

" Studies in Colour Reactions for Sugars. Part II. The Isolation of the Precursor and of the Blue Compound obtained by the Interaction of Thymol, Hydrochloric Acid and Ferric Chloride with Glucose ", by A. Bolliger, Ph.D., and A. J. Tow, M.Sc.

" The Chemistry of Osmium. Part I. The Redox Potential of a Trivalent-Quadrivalent Osmium Couple in Hydrobromic Acid ", by F. P. J. Dwyer, D.Sc., H. A. McKenzie, M.Sc., and R. S. Nyholm, M.Sc.

" The Spectrographic Analysis of Uranium ", by K. B. Mather, M.Sc., B.Sc. (Eng.). (Communicated by Professor O. U. Vonwiller.)

Lecturette.—A lecturette entitled " Consciousness and Instinct ", by A. S. Le Souef.

Film.—The film " Eruption of Ruapehu " was shown. The President thanked Dr. G. D. Osborne for having obtained the film on loan from Dr. Marshall at the A.N.Z.A.A.S. Conference in Adelaide.

October 2, 1946.

The six hundred and thirty-sixth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Fifty-six members and visitors were present. The minutes of the previous meeting were read and confirmed.

Popular Science Lecture.—It was announced that the lecture entitled " Triumph Over Pain : The Story of Anæsthesia " would be delivered by Dr. W. I. T. Hotten on Thursday, October 17th, 1946, which date was one day later than the centenary of the first use of ether in surgery.

Symposium.—The meeting was devoted to a symposium on " Tracer Elements ", which had been arranged by Dr. D. P. Mellor. The President introduced the subject, and the following short addresses were given :

" The Production and Measurement of Radio-Active Isotopes ", by N. A. Faull, B.Sc., A.Inst.P.

" The Use of Radio-Active Tracers in Biological Investigations ", by W. P. Rogers, Ph.D.

Before the meeting closed Mr. N. A. Faull demonstrated the Geiger Counter.

November 6th, 1946.

The six hundred and thirty-seventh General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Dr. A. Bolliger, was in the chair. Thirty-four members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : Michael Lederer.

Library.—The following donations were received : 86 parts of periodicals, two books and 59 back numbers.

The following papers were read by title only :

" The Mechanism Underlying the Formation of Aqueous Negative Binary Homoazeotropes ", by L. M. Simmons, B.Sc., A.A.C.I.

" The Elementary Existence Theorem for Differential Equations ", by W. B. Smith-White, B.A., B.Sc.

Commemoration of Great Scientists.—The following addresses were given :

" Boucher de Perthes. The Antiquity of Human Culture ", by Professor A. P. Elkin.

" Gottfried Wilhelm Leibnitz ", by Mr. W. B. Smith-White.

" Tycho Brahe ", by Mr. H. W. Wood.

" Valerius Cordus and the Pharmacopoeia ", by Dr. A. Albert.

December 4th, 1946.

The six hundred and thirty-eighth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Dr. A. Bolliger, was in the chair. Twenty-eight members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as ordinary member of the Society was read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : John Charters McPherson, Albert May, Cecil Rhodes-Smith, Margaret Crowley Weston.

Library.—The following donations were received: 113 parts of periodicals, 14 books and 50 back numbers.

The following papers were read:

"Some Minor Constituents of Eucalyptus Oils", by C. Ralph, M.Sc.

"The Redox Potential of the Tris-Orthophenanthroline Ruthenous Ion", by F. P. Dwyer, D.Sc., R. S. Nyholm, M.Sc., and J. E. Humpoletz.

"Complexes of the Diphenyl-methyl-arsine with Trivalent and Divalent Halides", by F. P. Dwyer, D.Sc., and R. S. Nyholm, M.Sc.

"Pyridine Co-ordinated Iodine Salts of Diazoamine Compounds", by J. R. Backhouse and F. P. Dwyer, D.Sc.

"The Colorimetric Estimation of Aromatic Hydroxy Compounds", by J. A. Friend, B.Sc.

"The Spectrographic Analysis of Steels", by S. C. Baker, M.Sc., A.Inst.P.

"The Uric Acid Content of the Feathers of the Muscovy Duck (*Cairina moschata*)", by A. Bolliger, Ph.D., and A. J. Tow, M.Sc.

"The Redox Potential of a Trivalent Osmium Couple in Hydrochloric Acid Solution", by F. P. Dwyer, D.Sc., J. E. Humpoletz and R. S. Nyholm, M.Sc.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman: Mr. H. O. Fletcher.

Honorary Secretary: Mr. R. O. Chalmers.

Meetings.—Six meetings were held during the year, the average attendance being eleven members and five visitors.

April 26th.—Address by Mr. J. M. Rayner on " Recent Advances in Geophysics in U.S.A."

June 21st.—Address by Dr. R. L. Aston on " The Use of Air-Photographs in Geology ".

July 19th.—Notes and Exhibits: By Miss Quodling: Method of measuring refractive indices of suitable minerals directly on Abbe-Zeiss Refractometer. By Dr. W. R. Browne: (*a*) Note on the discovery by Dr. S. W. Carey of a glacial series (striated pebbles, tillites and dolomitic varves) at the base of the Dundas series on King Island. These are the equivalent of the glacial series at Adelaide and Broken Hill; (*b*) Sericitized chiastolite in siliceous graphitic slate showing two grades of thermal metamorphism, the first gentle and the second more severe. By Mr. R. O. Chalmers: Large terminated crystal of precious tourmaline (green) from Kangaroo Island. By Mr. Fletcher: Upper Silurian trilobite remains tentatively referred to as *Encrinurus*, but of large size, from Borenore, N.S.W.

September 20th.—Address by Dr. W. R. Browne on " The Geological Age and Physiographic Relations of N.S.W. Bauxite and Laterite ".

October 18th.—Address by Mr. H. F. Whitworth on " The Commercialization of the Beach Sand Deposits of the North Coast of New South Wales ".

November 15th.—Address by Mr. F. N. Hanlon on " Summary of the Geology of the North-Western Coalfield, with Special Reference to the Gunnedah District ".

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